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68	formula XII	O	CO
	13	in	on
68	above arrow head preceeding formula XIII	Cos	COS
69	formula, line 2	$CO_2C_2H_5$	$CSOC_2H_5$
	,, XX	O_6	C_6
69	3rd equation	$C_6H_5NH{\cdot}CS\,NH_2$	$C_6H_5NHCS{\cdot}NH{\cdot}NH_2$
72	2	—carboxylic	4-carboxylic
72	XXIV	( )	O
73	8	sulphuetted	sulphuretted
77	23	N-carbothoxy	N-carbethoxy
99	4	Tarini	Tarani
99	13	IX	X
		X	IX
102	9*	Naphthylcarbazide.	Naphthylcarbamide

* from bottom.

OBITUARY NOTICE.

M. G. Srinivasa Rao, M.A , A.M.

(1884-1928).

Prof. M. G. S. Rao was born in Mysore in 1884. He received his University education in the Central College, Bangalore during 1901-4 obtaining the B.A. degree in the Physical Science of Madras University. Entering the Agricultural Department as an Assistant Chemist, he served for a short period under Dr. Lehman. In 1911 he was appointed Demonstrator in Chemistry in the Central College which provided him the opportunities to get the M.A. degree. Next year he was offered a foreign scholarship by the Mysore Government which enabled him to obtain higher training in Organic Chemistry under Prof. Kohler in the Harvard University. In 1916 he obtained the A.M., degree of the Harvard, returned home, and was offered the same year the chair of Organic Chemistry of the Mysore University. Prof. Rao was an able and lucid exponent of his subject and was a great favourite with his students. In him the poor students found the greatest friend. He had strong interest in sports of all kinds. Mr. Srinivasa Rao was an active member of the Chemistry Section of the Indian Science Congress. He was a Fellow of the Indian Chemical Society and served in the Council during 1927-28.

He contributed the following papers.

1. The *cyclo*propane series. Part IX. Nitro-*cyclo*-popane derivatives, in collaboration with Prof. Kohler (*J. Amer.., Chem. Soc.*, 1919).

2. 4-Methoxy-β-resorcylaldehyde from the roots of *Decalpis hamitonic* in collaboration with Mr. M. S. Iyenger (*Perf. Essen. Oil Rec.* 1923).

3. Substitution of Resorcinol derivatives. Part I. Nitro-derivatives of β-Resorcylic aldehyde in collaboration with C. Srikantan and M. S. Iyenger (*J. Chem. Soc.*, 1925).

Madyar Gopal Rao, B.A.

(1891-1928).

Madyar Gopal Rao was born in Mangalore in 1891. As a student, Mr. Gopal Rao was brilliant, taking the first place in every subject. He was the prize-man every year of his school and college career. He was a good debator and won in college, the prize for

public speaking. He had taste for music and was a good singer. Though physically disabled in leg, he was a keen sportsman. He graduated from the Presidency College, Madras and worked as research student of the Madras University under Dr. J. L. Simonsen for a few years. He published several papers on the problems of orientation. In 1920 he was invited by Dr. Simonsen when he was in Dehra Dun, to the post of Assistant Forest Chemist. He served in that capacity during 1920-24 and published several papers. His service was thereafter lent to the Khalsa College, Amritsar, where he served as Professor of Chemistry to the last. He was a keen and enthusiastic chemist and a perfect gentleman of genial disposition. He was an active Fellow of the Society and published in 1926 a paper on the essential oil from the flower-heads of *Perovskia antriplicifolia*, Benth, in the Society's *Journal*.

He contributed the following papers in collaboration with Dr. J. L. Simonsen.

1. Nitration of isomeric acetylaminomethoxybenzoic acid (*J. Chem. Soc.*, 1924).

2. Nitration of 2-acetylamino-3:4-dimethoxybenzoic acid and 3-acetylaminoveratrole with Charles Gibson (*J. Chem. Soc.*, 1917).

3. Nitration of 5- and 6-acetylamino-3:4-dimethoxybenzoic acid and 4-acetylaminoveratrole (*J. Chem. Soc.*, 1918).

4. Synthesis of 1:6-dihydroxy-2-methylanthraquinone (*J. Chem. Soc.*, 1921).

5. Oils and fats from the seeds of Indian forest trees (*Indian Forest Records*, 1921).

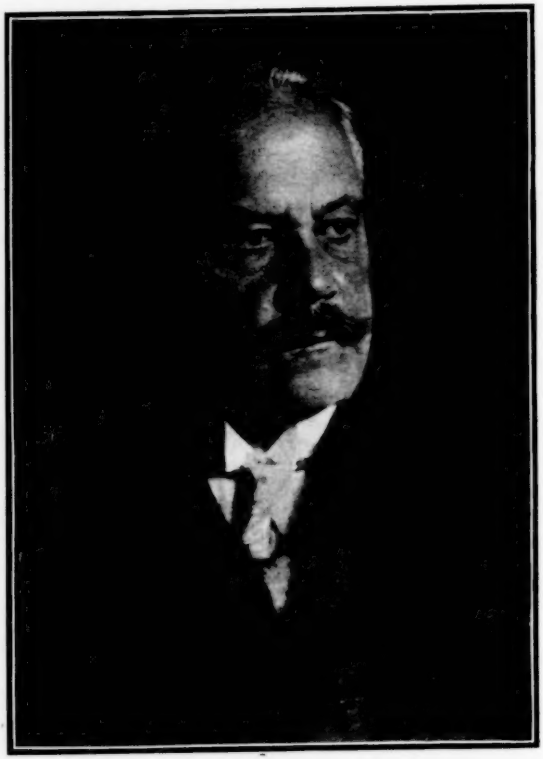
6. Essential oil from *Blumia Malcomiee* (*Indian Forest Records*, 1921).

7. The constituents of Indian terpentine from *pinus longifolia*, Roxb. (*J. Chem. Soc.*, 1923).

8. The constituents of some Indian essential oils (*Indian Forest Records*, 1922).

9. Oils and fats from the seeds of Indian forest plants. Oil from the seeds of *Salvia plebeia*, R. Br. (*Indian Forest Records*, 1924).

10. Essential oil from the flower-heads of *Perovskia antriplicifolia*, Benth (*J. Indian Chem. Soc.*, 1926).



PROF. ARNOLD SOMMERFELD
[Elected First Honorary Fellow of the Society]

Recent Researches on the Biochemistry of the Nitrogen Cycle.*

By Gilbert J. Fowler, D.Sc., F.I.C.

If the ordinary individual commonly known as 'the man in the street' were asked which was the most valuable among the elements, he would probably mention gold, or possibly platinum. In India silver is highly valued. None of these, however, is indispensable. To anyone with an elementary knowledge of chemistry oxygen might be singled out since without it human life cannot exist. At the same time phosphorus, carbon and calcium, sodium and chlorine might put forward their claims, but in the end the most precious element would be found to be nitrogen since it differs from all others in the fact that in the free state, as it exists in unlimited quantities in the atmosphere, it is inert and incapable of easily entering into combination as does oxygen. Consequently it has to be jealously watched lest it should go back to its free and inert state and although still present be unavailable. When a plant or any other living thing is burnt its ashes remain and can be returned to the soil. The hydrogen is still present and available as moisture, the carbon while dissipated as carbon dioxide is readily brought back into the cycle of life by any green plant, in the course of a few hours of sunlight.

Nitrogen, however, is different, once it has escaped into the air it can only be recovered by certain forms of life which are not always immediately present, and whose action requires a liberal provision of space, time and material.

Even nitrogen which is present in the soil in the form of nitrates, or in various complex compounds in the sewage of cities tends ultimately to reach the sea whence it is only partially recoverable as fish or sea-weed.

* Presidential Address to the Indian Chemical Society, given at the Presidency College, Madras, January 5, 1923.

There has therefore been up till recent times a real danger pressing upon humanity, *viz.*, the conversion of available forms of nitrogen into unavailable, and the consequent loss of soil fertility involving rapid reduction in the food supply of the world.

Some seventy years ago Liebig wrote as follows of ancient Rome:

"The sewers of the immense metropolis of the Ancient World, engulfed in the course of centuries the prosperity of the Roman peasants and when the fields of the latter would no longer yield the means of feeding her populations, these same sewers devoured the wealth of Sicily, Sardinia, and the fertile lands on the coast of Africa."

Describing mediaeval agriculture in England Prothero writes: "There was little to mitigate, either for men or beast, the horrors of winter scarcity. Nothing is more characteristic of the infancy of farming them the violence of its alterations. On land which was inadequately manured, and on which neither field-turnips nor clovers were known till centuries later, there could be no middle course between the exhaustion of continuous cropping and the rest cure of barrenness." Considerations such as these, applied to the conditions existing in his time, led to the famous warning of Sir William Crookes in 1898 as to the crying need for nitrogen conservation. Happily the warning has been needed and modern chemical technology has come to the rescue, and by the expenditure of very considerable physico-chemical energy in the various processes of what is known nitrogen fixation has succeeded in obtaining nitrogen from the air in simple combinations suitable for use as fertiliser such as ammonium salts, nitrates, calcium cyanamide etc.

These modern methods of recovery of nitrogen from the air have so developed especially since the War that according to the latest statistics there would seem to be little danger of nitrogen famine. In fact there is a possibility of a glut of nitrogen compounds. Nevertheless the problem is not, even so, entirely solved since it has been found that mineral nitrogen in the form of ammonium compounds, and nitrates, or amino compounds such as cyanamide and urea, are not fully adequate to meet the needs of plants. Just as nitrogen in the form of gelatine was long ago found inadequate to supply the requirements of human food, and as all modern researches have indicated, certain accessory substances are necessary to maintain proper nutrition, so in the case of plants it has been found by age long practical experience that something more than mineral nitrogen

is required for healthy crop development. The experience of forty centuries of Chinese agriculture, and of more than half a century of scientific experiment at Rothamsted, has been confirmed by the researches of the Madras Department of Agriculture working in conjunction with the Deficiency Diseases Inquiry under Lt. Col. McCarrison, who together have shown that in order to obtain increased crop yields and to secure seed which will give a vigorous crop in the next generation, organic manure is essential. McCarrison has shown by feeding tests that wheat grown on a crop which received cattle manure was 15 per cent. more nutritous than wheat produced from a crop manured with artificials alone. Thus we find that the problem of agriculture and of nitrogen conservation cannot at present be met by the provision of mineral compounds on however vast a scale modern technology can produce them. In India there is the further handicap of the poverty of the peasant and his lack of scientific knowledge which, even if he can afford modern fertilisers in quantity, would make it almost certain that much of them would be wasted by inefficient application. The problem is still essentially one of biochemistry and in seeking for a subject for this address it seemed to me that it would be of interest to bring together the advances in our understanding of the biochemistry of nitrogen during the years which have elapsed since the last meeting of the Science Congress in Madras when I had the pleasure of addressing the members of the Chemical Society of the Presidency College on the methods and aims of the biochemist in India. About that time also in a number of the Journal of the Indian Institute of Science I tried to collect such knowledge as I possessed on the subject of the conservation of nitrogen and to indicate possible lines of research. It is a great source of satisfaction to me that in the Department of Biochemistry at Bangalore under my successor Dr. Norris and his coworkers, the lines of work which I had hoped might be pursued, in the interests of the scientific foundations of agricultural chemistry, have been most brilliantly and adequately taken in hand and many of the researches to which I shall have occasion to refer have either been made in the Bangalore laboratories or by students trained there.

I am also glad that Prof. Donnan in his stimulating British Association address on the "Mystery of Life," advocated the study of the biochemistry of unicellular organisms, as the shortest path to the solution of many fundamental problems. I have long held that view.

It will be convenient to review the subject under the following heads:—

Sources of organic nitrogenous fertilisers.
Losses of nitrogen.
Protein formation and decomposition.
Nitrification.
Nitrogen fixation.

Sources of nitrogenous organic fertilisers.

Oil-seed cakes.—The problem of the utilisation of nitrogen in oil-seed cake still remains. In certain parts of the country, notably the Bombay Presidency castor cake is readily sold at good prices and there is ample experience to show that it is an excellent fertiliser having the highest percentage of nitrogen in any oil-cake. It has some possibilities as a food-stuff and experiments in this direction have been made at the Harcourt Butler Technological Institute, Cawnpore, but the expense and difficulty of extracting both the oil and the ricin make it questionable whether it is worth while to pursue investigation in this direction especially as the prepared cake is not very readily taken by cattle.

I learn that in the northern portions of the Madras Presidency groundnut cake finds ready application as a cheap and useful manure.

Mahua seed cake.—Some interesting results have been obtained in regard to this material both at Pusa and at Cawnpore. At Pusa it has been shown that preliminary fermentation of the cake especially in presence of charcoal renders the nitrogen much more available. At Cawnpore it has been found that the mowrhin present in the cake is certainly detrimental to the growth of plants if the cake is used without any previous treatment and if the crop is planted immediately after the application of the cake to the soil. On washing out the mowrhin with water, however, the residual cake gives very good results, the effect being striking in regard to the quality of the flowers and seeds. The value of preliminary treatment in this way will depend on whether a use can be found for the extracted mowrhin, which is a saponin and has some possible uses as a hair wash and as an ingredient of ordinary soap. The mahua cake can be used without any preparation if added to the soil just before the monsoon and if sufficient time is allowed for the rain to wash out the detrimental constituent, or if a certain amount of charcoal to the

extent of 5 per cent. of the cake used is mixed with it together with 25 per cent of soil and the compost allowed to ferment before use.

Cowdung.—It appears to be assumed in many quarters that it is useless to expect the Indian agriculturist to use cowdung otherwise than as fuel.

Experiences at Gurgaon have shown that this like many other pessimistic assertions concerning this country is by no means necessarily true and that a little intelligent education and strenuous but sympathetic work in the villages can remove this great barrier to progress in Indian agriculture.

Moreover there are great possibilities in the economic use of such cowdung as is available. Instead of allowing it to rot in masses without any scientific supervision, or to be mixed without care with miscellaneous plant and other residues, it is possible by careful management to get far more value out of it when used as a ferment than when it is used in bulk as a manure. If waste vegetable matter is piled in heaps and thoroughly moistened with a decoction of cowdung and water the necessary bacteria present in the cowdung are evenly distributed over the waste materials.

In this way an active mass of fermenting compost is obtained which can be used as an activator for further quantities of raw material, the whole being kept moist and quantities of soluble nitrogen being added preferably in the form of diluted cow's urine. By a little systematising the process can be made continuous, at one end of the heap well rotted compost can be taken away while fresh material is added and mixed at the other end, the whole being periodically turned over from end to end. In this way the original method of Richards and Hutchinson now known as 'Adco Process' is greatly accelerated. The value of this use of activator and diluted cowdung is mainly to reduce the time necessary for production of the fertiliser, but also incidentally it would appear that the product contains a greater percentage of nitrogen than is possible by less elaborate methods. Even when the raw material is simply rotted in heaps very valuable results are obtained and it is stated in a recent paper issued by the Director of Agriculture and the Agricultural Chemist of Bengal that for the first time in its history the Government Farm at Dacca has had an ample supply of manure. If this can be said of a Government Farm what must it mean to the whole of India where resources in knowledge and materials are in general so much less.

Activated Sludge.—I have already quoted the warning words of Liebig on the wastefulness of the water carriage system of sewage disposal.

In a recent address to the First International Congress of Soil Science in Washington, Sir John Russell repeats the estimate of the value of the excreta of the population of the United Kingdom which he gave in war time for a population of 45·2 millions, as amounting to a sum of £17,500,000 per annum or 7*s.* 9*d.* *i.e.* Rs. 6 per head. Very little of this finds application in agriculture.

On the other hand for more than forty centuries the patient farmers of China have maintained the fertility of their vast and thickly populated country without the importation of a ton of artificial manure. This has been done through the intelligent use of composts of vegetable matter and the careful conservation of human excreta.

So great is the value attached to human excreta as manure that the city of Shanghai has been accustomed to receive a payment of £40,000 per annum from a contractor for the privilege of removing night soil from the houses. In adding to this payment the contractor bears all collection costs, so that the city has no conservancy charges. The total value of night soil in Shanghai thus works out at something like Rs. 2 per head. This figure includes but little of the nitrogen in solution in urine which goes to make up Sir John Russell's figure of Rs. 6. All of the materials for which the contractor pays so liberally is conveyed in a liquid state by boats along the multitudinous creeks of China, to be used with meticulous care by the farmer. The methods in use in India form a somewhat melancholy contrast to the scientific thrift of the Chinese. Even where in the country certain fields are set apart for purposes of nature no effort is made to incorporate the excreta with the soil so that much of the manurial value is lost, and highly insanitary conditions are created owing to the infection carried by flies and other insects which alight on the exposed excreta. The fact that children, even in towns, are not trained to sanitary habits is a cause of loss and danger to the community. Where pail conservancy is practised the methods of trenching employed, even where the contents of the trench are ultimately used for manure, result in great loss of nitrogen. Apart from this, in many places, caste prejudice is so strong that no product of any sort, if ultimately derived from nightsoil, will be touched by the cultivator.

This caste prejudice can in these days hardly claim religious sanction, while the bathing ghats at Benares are being increasingly polluted by the sullage from that holy city, and when the whole of the sewage of Cawnpore for example is allowed to pass unpurified into the Ganges.

The following extract from a note by Mr. Asharfi Lal Gupta, Executive Officer, Municipal Board, Benares, dated 17th April, 1925, is a striking comment on this state of affairs. Mr. Gupta writes:—

"It is in the interest of sanitation as well as religious sentiment to save these waters from being polluted and rendered unfit for bathing. Rivers are not polluted even in countries where they are not considered holy or sacred by anybody; for example, in England and Ireland, where no one worships any river, there are Rivers Pullution Prevention Acts under which any act by which the river water is polluted is an offence. Very probably at least one reason for investing such waters with "religious sacredness" here in India by long continued tradition, was the very sanitary purpose of preventing persons from befouling them, but, unfortunately, this aspect of the question has been completely forgotten by the public."

In spite of the appalling waste involved one may have some sympathy with those who are reluctant to use any form of human waste as manure. When used without proper preparation it is an exceedingly unpleasant substance to deal with. The advent of the activated sludge process which briefly stated depends on intensive biochemical oxidation makes it possible to use such material without any nuisance with the production of an inoffensive brown humus containing 5 to 6 per cent. of nitrogen of great availability and a clear odourless solution of nitrates, which can be used for irrigation without danger of nuisance or of rendering the land "sewage sick."

During the last ten years striking progress has been made in the development of the activated sludge process. Great cities such as Milwaukee and Chicago have expended millions of dollars on sewage works and in the near future they will be followed by Indianapolis and a portion of New York. Birmingham, Manchester and London have large schemes in hand and in this country Bombay is actively preparing plans for the treatment of a portion of its sewage by this process. Shanghai which formerly, as I have said, obtained an income of about Rs. 2 per head by the sale of its night soil, is now gradually bringing the whole of its human wastage to be treated in activated sludge plants and the Chinese agriculturist is gradually

accustoming himself to the use of the sludge instead of the offensive crude night soil which he hitherto valued so highly. Bulk for bulk the Sanitary Chemist to the Shanghai Municipality reports that comparative analyses of a large number of samples of sludge and ordure show that an average sludge containing six per cent. of nitrogen on the dried matter if de-watered to the condition of spadable mud will provide 2½ times as much available nitrogen and other constituents of manurial value as the same bulk of ordure. It is much better if possible to use activated sludge in the semi-liquid state as is done by the Chinese farmer, who will be able to boat the material about the creeks of China as he used to convey his horrible cargoes of liquid nightsoil. In this country river creek communication is infrequent, so that transport of this material, if it cannot be used on the site of a works, will necessitate preliminary drying. For 9 months of the year this should not be difficult and in any event methods are at present under consideration for economically drying it by artificial heat. The advantage of this would be the elimination of infection such as hookworm which is a natural cause of anxiety to Directors of Public Health.

That the drying of activated sludge is no longer matter of experiment, although capable of great improvement, is shown by the published reports from Milwaukee where they have now created an assured market for 30,000 tons of dried sludge having an annual value of £100,000 sterling. The night soil of India at present, instead of being a source of wealth as it is in China and it will shortly be in the United States and in Europe, is a menace and a nuisance. It may be hoped that its proper utilisation may be one of the subjects for consideration by the Imperial Research Council recommended by the Agricultural Commission.

Losses of Nitrogen.

It is well known that under certain conditions the nitrogen present in organic matter which would otherwise enter usefully into the cycle of growth is converted into free nitrogen by certain chemical changes and thus becomes virtually lost to agriculture. The mechanism of these changes does not seem to be so clearly understood as was assumed at any rate by some of us. A frequent explanation given of the loss of nitrogen is that it results from the action of amino compounds with nitrites according to the familiar

reaction with urea. Upon investigation however using solution of a concentration comparable to those likely to be present under natural conditions very little evidence was found of such a loss. Recent researches of water logged soils by V. Subrahmanyan, a distinguished student of Bangalore and Rothamsted, now on the staff in the Department of Bio-chemistry at Bangalore, show no evidence of any net loss of nitrogen although the combinations in which it is present undergo change. Researches at Bangalore on the conditions of loss of nitrogen from activated sludge indicate that this only takes place if the material is brought in contact with nitrates in an imperfectly oxidised state. In fact it has been proposed, as a methed of distinguishing between sludge which is in a well conditioned or imperfectly conditioned state, is to ferment the material in contact with a diluted solution of nitrates when if the sludge tends to be at all putrefactive nitrogen will be evolved. This would indicate that good aeration is desirable if the loss of nitrogen is to be avoided.

I cannot recall any evidence of loss of nitrogen in the form of gas in any natural process other than through the reduction of nitrates. Loss occurs in this way undoubtedly in the so-called contact bed used in the purification of sewage effluent where the bed is alternately filled and emptied. During the period when the bed stands empty there is a formation of nitrate and when it is standing full this nitrate is reduced by the organic matter of the effluent with resultant loss of nitrogen in the free state.

It is well known that there is often considerable loss of nitrogen during the storage of farm yard manure. The origin of this has never been quite clear and Niklewski in a recent paper contends that the loss of nitrogen from manure heaps is due to formation of nitrate in semi-dry portions of the heap and inter-action of this nitrate with other portions. He states that there is no loss of nitrogen if an ample supply of ammoniacal nitrogen is present as urine so that the process of nitrification is checked.

It is evident that more research is needed on this question. It was at one time thought that free nitrogen was given out from septic tanks ; but although there is change in the formation of combination there is no evidence of actual loss in the septic tank process.

Akin to the conditions in a septic tank are those on water-logged paddy soils and yet from them loss of nitrogen has been observed.

Subramanyan has recently shown that there is a gradual absorption of dissolved oxygen from water which covers alluvial soil the amount of dissolved oxygen being naturally most at the surface and least in immediate contact with the soil. It would appear quite likely from this, and from other evidence connected with the operation of activated sludge tanks, that nitrates may be formed in the upper portion of the aqueous stratum and reduced to free nitrogen at greater depths below the surface. It has been suggested to me consequently that the depths to which paddy fields may be flooded is one of serious agricultural importance on account of these possibilities of nitrogen loss. This point was left somewhat obscure by the researches of Harrison and Subramania Ayyar. In their experiments copper sulphate was added in order to eliminate the action of the surface film around it: but it would appear possible that oxygen of the air can take part and nitrate be formed without the intervention of green algae.

Protein Formation and Decomposition.

This section comprises some most interesting problems involving the bio-chemistry both of the soil and of the plant. In the soil are many forms of life-bacteria, fungi, algae, protozoa, not to mention worms, all working together to produce food for the plant. The investigation of the part played by these various organisms is difficult since it cannot be stated that the behaviour of each separately correctly represents the behaviour of each when associated together in the soil.

New methods of investigation using samples of the unaltered soil have been devised by Winogradski and others which offer considerable promise. In this connection the activated sludge tank affords an interesting weapon of research since we have in the activities of the bacterial sludge to which the name activated sludge is given a condensed picture of what happens in arable soils. I make this statement after consultation with Sir John Russell and Mr. Cutler at Rothamsted where special investigations have been made on the micro-flora of the activated sludge tank. Interesting work has also been done by Lockett in Manchester and Swaminathan at Bangalore to which reference will be made later.

There is no doubt that protein is built up in the soil from simpler nitrogenous compounds. Such activity is made use of in the ADCO

process for producing artificial farm yard manure by fermenting mineral compounds of nitrogen with carbonaceous matter. Rege in Bangalore made a number of interesting laboratory experiments in the endeavour to increase the rate of what may be called the demineralisation of ammonium compounds by building up an active mass of the necessary organisms. It would take too long to go into the details of these experiments. But by using a mixture of easily fermentable carbohydrate such as powdered grass together with ammonium sulphate and calcium carbonate and with activated sludge as a source of the necessary organisms it was possible by suitable technique completely to convert mineral into protein nitrogen in 24 hours. This technique has since been applied to the making of composts.

Further work in this direction by Rege at Rothamsted showed that among the most active agents in breaking down carbohydrate matter were certain moulds some of which can thrive at a temperature as high as 60°. This also has been confirmed by practical experience.

Work at Rothamsted has also shown that only certain forms of carbohydrate tissue lend themselves to this process, plant residues being less readily broken down in proportion to the degree to which lignification has taken place.

In Rege's laboratory experiments it was observed that between each addition of ammonium sulphate and carbohydrate there was evidence of the formation of nitrate which afterwards disappeared without loss of total nitrogen, being apparently worked up into protein compounds. This observation is of interest in regard to our theories as to how plants build up their protein from the nitrogen supplied to them. One school of thought appears to assume that the source of all nitrogen metabolism, other than that of the leguminous plants at any rate, is nitrate-nitrogen in some form and numerous chemical hypotheses have been made by Baly and others indicating how proteins may be built up by a combination of the possible reduction products of nitrates and the derivatives of formaldehyde.

There is evidence, however, that the plant can absorb nitrogenous compounds other than nitrates and we are brought here to the consideration of plant vitamines or auximones as they were termed by the late Professor Bottomley.

The experiments already referred to carried out by the Agricultural Department of Madras, would indicate that plants need for

their proper nutrition certain complex products which are difficult to supply otherwise than through the agency of organic manures. It was suggested in my 1920 paper that the extraordinary effectiveness of activated sludge as a manure might be due to the presence of the necessary bacteria in a nidus of nitrogenous organic matter suitable for the production of auximones. Since that time definite investigations by Bartow and his colleagues of the illinois Water Survey have shown that numerous organic bases and nucleo-proteids can be extracted from activated sludge.

The food products for the plant are mainly due to bacterial activity, and soil fertility is very commonly associated with a high bacterial count and any conditions tending to a limitation of of bacterial activity are looked upon as inimical to fertility. In this connection the rôle of protozoa in the soil has received considerable attention. Their undue multiplication would seem to be detrimental both by withdrawing a certain amount of available plant food into the structure of their own bodies and at the same time by their direct attack upon the bacterial population. From these considerations have arisen the methods of sterilisation of the soil developed by Russell and Hutchinson and which have been applied with extraordinary success more particularly to the growing of tomatoes. By the application of carbolic acid to the soil at the rate of $2\frac{1}{2}$ tons per acre it has been possible to raise the yield of tomatoes in certain places from 28 tons to 43 tons per acre. Carbolic acid is expensive and other cheaper antiseptics have been sought for among them chloro-dinitrobenzol which is found to be 7 times as powerful as carbolic acid.

There is still some difference of opinion as to whether the action of antiseptics is entirely due to their effect upon the protozoal life of the soil or whether they may not act in certain cases as stimulants to bacteria some of which are capable of utilising substances such as carbolic acid as food. There is an interesting task here for the organic chemist to devise differential antiseptics and a good deal of work has been done in this direction by Fairbrother and Renshaw.

Summarising the question of the rôle of protazoa in the soil and in the activated sludge tank, it would appear that they are only detrimental when present in undue proportion. Under such circumstances it may be possible as has been shown by Swaminathan at Bangalore to reduce their number and at the same time increase the number of bacteria by suitable applications of methylene blue.

Lockett in Manchester has shown that the different species of protozoa found in activated sludge are indicative of the condition of the sludge.

The rôle of fungi in the soil has been referred to in connection with the work of Rege on carbohydrate decomposition. Norris and Thakur have shown that certain fungi secrete an amidase capable of breaking down the products of protein decomposition finally to ammonia. Subramaniyan has also investigated the aminase present in various Indian and Rothamsted soils capable of breaking down amino compounds in the absence of living bacteria.

Nitrification.

A considerable amount of work designed if possible to increase the rate of the conversion of ammonia to nitric acid by bacterial action has been done of recent years. Among the most extensive of these researches are those of Boullanger in France who endeavoured to apply the resources of modern science to improve the yield of nitrates as compared with the processes evolved during the time of the Napoleonic wars. Boullanger's experiments were carried out both in the laboratory and on a semi-technical scale and he used ordinary nitrifying filters the most satisfactory material for which he found to be natural pozzuolana in granules size of cherry stones. He found it necessary to begin the process of intensive nitrification very gradually, since the nitrifying organism is paralysed by excessive ammonia. Nitrates also have an inhibitory action at the beginning of the process. By employing a very careful and special technique he succeeded in obtaining a regular output of a solution up to 12 per cent. of calcium nitrate. The cost, however, of the process was not economical except as a war emergency. Other work has been done by Joshi at Pusa and by a number of workers at Bangalore, the latter employing the activated sludge principle, *i.e.*, moving the organisms through the liquid instead of passing the liquid over a stationary mass of organisms. It was not found possible, however, to obtain a concentration of calcium nitrate in the laboratory by this method beyond $7\frac{1}{2}$ per cent. The work was of considerable practical interest from the point of view of the control of activated sludge plants and one result obtained incidentally under the direction of Dr. Norris deserves special attention. It was found in the course of the experiment that the addition of animal charcoal

to the oxidising mixture not only greatly accelerated the rate of nitrification but even in the practical absence of bacteria brought about considerable formation of nitrate. This result although in confirmation of the experiments of Warburg is contrary to the general experience of many workers prior to the classic researches of Schlocsing and Muntz and the later researches of Russell and Smith. This subject deserves further study.

Nitrogen Fixation.

The well-known fact that certain bacteria are able to bring gaseous nitrogen back into the life has always been a bio-chemical mystery. Personally I have for some reason inclined to the view that a direct combination of oxygen and nitrogen was brought about resulting in the production of nitrates from which protein could be synthesised in the manner already indicated. Recent publications by Norris and Ranganathan indicate that the nitrogen fixing organism *azotobacter chroococcum* prefers the Haber process of nitrogen fixation to the Scandinavian in as much as ammonia is the first product recognised. It should be possible by intensive methods to increase the rate of nitrogen fixation by biochemical agencies just as it has been possible to accelerate other nitrogen conbinations and there is evidence of such fixation of nitrogen in certain recent large scale work on the making of composts from sunnhemp.

The subject of the inoculation of soils with nitrogen fixing organisms is still attracting attention. Stoklasa speaks very favourably of a special material produced by inoculating sterile turf with suitable organisms and adding finely powdered phosphate and a small percentage of kainit a mixture which he terms humophosphate, large quantities of which have been used with good results in Czeko-Slovakia, increases of the crop yield from 30 per cent. to 130 per cent. being reported.

Russell recommends the inoculation of seed by special cultures grown in milk.

One very interesting result which was given out from Rothamsted in recent years is that of the importance of traces of boron in the soil in establishing the necessary link between symbiotic nitrogen fixing organisms and the corresponding plant.

It appears from the researches of Bristol-Roach that algæ are not capable themselves of fixing nitrogen, as some observers believed,

but they do in some way increase by their presence the activity of ordinary nitrogen fixing organisms.

General.

In the time at my disposal it has only been possible to deal in a very cursory manner with a very large subject. But sufficient has been said to indicate that the problems of the soil and especially of what is known as the nitrogen cycle afford an infinity of research material for the chemist. It is of interest to note that a large proportion of the Directors of Agriculture in this country began their careers as chemists and therefore the memorandum which has been sent down to the various universities of India at the instance of the Royal Commission on Indian Agriculture urging that the Universities should interest themselves in the problems of agriculture is one to which the Indian Chemical Society should surely give heed. In other lines of activity it is necessary properly to allocate the work of each individual. In chemical technology there has been much discussion as to the relative position of the chemist and the engineer. Something of the same relationship has to be discussed in considering research connected with agriculture. It has been recently stated by an American writer that we are forced to define an agriculturist as an organic chemical manufacturer. If this be so we may recall that in a large chemical factory there is, or should be a research laboratory where problems are investigated bearing on the work of the factory, but for the moment untrammelled by immediate exigencies of profit making. Such work which mainly regards the future should be done in a every up-to-date concern. May we not hope that the chemical laboratories of the Indian Universities may play some such part in relation to India's greatest industry.

Investigations on the Colloidal Behaviour of Antimony Pentoxide.

By S. Ghosh and N. R. Dhar.

Although a considerable amount of work has been done on vanadium pentoxide sol, hardly any research has been carried on with a sol of antimony pentoxide. Delacroix (*Bull. Soc. Chim.*, 1899 (*iii*), **21**, 1049; 1901, **25**, 288), and Senderens (*ibid*, 1899 (*iii*), **21**, 47) believed that the product obtained by the hydrolysis of antimony pentachloride existed in the state of true solution. In recent years, Jander and Simon (*Kolloid Zeit.*, 1918, **23**, 122; *Z. anorg. Chem.*, 1923, **127**, 68) studied the vapour pressure and adsorption isotherms with hydrated antimony pentoxide.

We have shown that freshly prepared sols of silicic, vanadic and tungstic acids exist partly in the molecular condition and these dissolved molecules in course of time polymerise to form bigger aggregates. We have also observed that this process of polymerisation is facilitated by hydrogen ions and retarded by OH ions. These conclusions are supported by the measurements of viscosity, electric conductivity and stability towards electrolytes.

As no research regarding the colloidal behaviour of antimony pentoxide seems to have been carried on and as vanadium and antimony occur in the same periodic group we have investigated the sol of antimony pentoxide from different points of view.

Preparation of the Sol.

Dilute nitric acid was added to a contentrated solution of potassium antimonate at 20° and the precipitated antimonic oxide washed free from nitric acid, when the oxide began to pass into a colloid. The whole of the precipitate and some of the colloid are now kept in a parchment bag for dialysis. As the dialysis proceeded it was observed that some antimonic acid appeared in the dialysate. After ten days' dialysis a slightly turbid, negatively charged sol of antimony pentoxide was prepared. The following results were obtained on the coagulation of antimony pentoxide sol.

TABLE I.

Concentration of the sol = 0·95 grm. of Sb_2O_5 per litre; 3 c.c. sol made up to 6 c.c.; Time = 1 hour.

Electrolyte.	Amount to coagulate in c.c.	Precipitation values.
LiCl N/10	2·20	0·0367
NaCl N/10	2·00	0·0333
KCl N/10	1·30	0·0217
NH_4Cl N/10	1·30	0·0217
HCl N/10	1·30	0·0217
NaOH N/10	2·50	0·0417
CH_3COONa N/10	2·00	0·0333
$BaCl_2$ N/100	0·70	0·0012
$Al(NO_3)_3$ N/333·3	0·225	0·00013
$Th(NO_3)_4$ N/333·3	0·35	0·00017
Congo red M/1000	0·55	0·00009

Hence the coagulating powers of different electrolytes are in the following decreasing order:—Congo red > $Al(NO_3)_3$ > $Th(NO_3)_4$ > $BaCl_2$ > KCl, HCl, NH_4Cl > NaCl, CH_3. COONa > LiCl > NaOH.

It will be seen that the Schulze-Hardy law is applicable to the coagulation of antimony pentoxide sol by different electrolytes, the exceptions being congo-red, which is highly adsorbed by the sol and thorium nitrate, which shows abnormal behaviour with several other negatively charged sols.

It has been observed that the sol becomes positively charged when quantities of congo-red, $Al(NO_3)_3$, and $Th(No_3)_4$ greater than their precipitation values are added to the sol.

In the following table the results are recorded when the sol of antimony pentoxide is coagulated by electrolytes at various concentrations of the sol:—

Sol A = 3 c.c. made up to 6 c.c.

Electrolytes	Amount of electrolyte to coagulate in c.c.		
	Sol 4A/3.	Sol A.	Sol A/2.
KCl N/10	1·50	1·30	1·10
HCl N/10	1·45	1·30	1·10
NaOH N/5	1·25	1·25	1·20
$BaCl_2$ N/100	0·85	0·70	0·35
$Al(NO_3)_3$ N/333·3	0·30	0·225	0·12

The foregoing table shows that the greater the concentration of the sol the greater is the amount of electrolyte necessary for coagulation irrespective of the valency of the cation. The sol, therefore, follows our dilution rule.

The sol was coagulated with mixtures of KCl and $BaCl_2$, KCl and HCl, and NaCl and NaOH and the following results were obtained:—

Amount of sol taken each time=3 c.c.

N/10 KCl added in c.c	N/100 $BaCl_2$ necessary for coagulation in c.c. Added.	Calculated.	Difference.	% Difference.
1·30	0	—	—	—
0	0·70	—	—	—
0·2	0·60	0·59	—0·01	1·7
0·4	0·50	0·48	—0·02	4·2
0·6	0 42	0·38	—0·04	10·5
0·8	0·25	0·27	+0·02	7·4
1·0	0·20	0·18	—0·02	11·1

N/10 HCl added in c.c.	N/10 KCl necessary for coagulation in c.c. Added.	Calculated.	Difference.	% Difference.
0	1·30	—	—	—
1·30	0	—	—	—
0·20	1·05	1·10	—0·05	4·5
0·40	0·90	0·90	0	—
0·60	0·75	0·70	+0·05	7·1

N/10 NaOH added in c.c.	N/10 NaCl necessary for coagulation in c.c. Added.	Calculated.	Difference.	% Difference.
0	2·00	—	—	—
2·5	0	—	—	—
0·2	1·90	1·76	0·14	7·9
0·4	1·95	1·68	0·27	16·1
1·6	0·80	0·72	0·08	11·1

The results in the above tables show that practically additive values are obtained when the sol is coagulated by mixtures of KCl and $BaCl_2$ or HCl and KCl. Slight ionic antagonism is observed

when the sol is coagulated by NaCl and NaOH. The phenomenon of acclimatization has also been studied with this sol and the following results are obtained:—

Amount of sol taken = 3 c.c. Volume = 6 c.c.

Electrolyte.	Amount to coagulate.		
	Amount added every hour.	Added all at once.	Added slowly.
$BaCl_2$ N/160	0·1 c.c.	0·70 c.c.	0·65 c.c
$Al(NO_3)_3$ N/666·6	0·1 c.c.	0·45 c.c.	0·40 c.c.

It will be observed that this sol does not develop the phenomenon of positive acclimatization.

Hence antimonic acid sol behaves normally towards dilution, and mixtures of electrolytes and does not show positive acclimatization and cannot appreciably adsorb similarly charged ions from electrolytes like KCl, $BaCl_2$, $Al(NO_3)_3$ etc.

We have investigated the change in viscosity of the sol in presence of KCl, HCl and NaOH and the following results are obtained.

Temperature 30°.

	Viscosity.
Water	0·00803
19 c.c. Sol + 1 c.c. water	0·00813
19 c.c. Sol + 0·1 c.c. N/10 NaOH + 0·9 c.c. water	0·00803
,, + 0·5 c.c. N/10 NaOH + 0·5 c.c. water	0·00826
,, + 1·0 c.c. N/10 NaOH	0·00829
,, + 0·1 c.c. N/10 HCl + 0·9 c.c. water...	0·00807
,, + 0·5 c.c. N/10 HCl + 0·5 c.c. water ...	0·00829
,, + 1·0 c.c. N/10 HCl	0·00832
,, + 0·1 c.c. N/10 KCl + 0·9 c.c. water ...	0·00806
,, + 0·5 c.c. N/10 KCl + 0·5 c.c. water ...	0·00827
,, + 1·0 c.c. N/10 KCl	0·00834

The above table shows that there is first a decrease of viscosity in presence of traces of NaOH, HCl and KCl and then the viscosity increases as more of the electrolytes are added. We have shown

that traces of alkali produce an increase in the viscosity of the sols of silicic, tungstic and vanadic acids, and that OH ions in traces markedly sensitize these sols towards the action of electrolytes. We have also observed that the sols of silicic, tungstic and vanadic acids show marked increase in viscosity, great decrease in electrical conductivity and appreciable change in p_H values on ageing. In this paper we have also studied these properties with antimonic acid on ageing and find that these change vary little in comparison with that observed with silicic, vanadic and tungstic acids. The results obtained with antimonic acid are recorded in the following table:—

Temperature 30°.

Date.	Conductivity.	p_H value.	Viscosity. (19 c.c. Sol + 1 c.c. water).
15th August, 1928	0·00306	4·2	0·00813
19th ,, ,,	—	—	—
20th ,, ,,	0·00302	—	—
30th ,, ,,	0·00300	—	—
13th September, 1928	0·00298	4·3	0·00821

The influence of boiling and ageing on the stability of this sol towards electrolytes was also determined and the following results were obtained:—

Concentration of the sol—3 c.c. of the sol taken each time.

Volume = 6 c.c. Time = 1 hour.

Electrolyte.	Amount to coagulate in c.c. Fresh sol.	One month old sol.	Boiled sol.
KCl N/10	1·30	1·30	1·25
$BaCl_2$ N/100	0·70	0·70	0·70

It will be observed that there is practically no change in the stability of the sol either on keeping or boiling.

It is well known that some sols when precipitated by certain electrolytes can pass into the colloidal condition again on washing. Thus Linder and Picton (*J. Chem. Soc.*, 1905, **87**, 1926) peptised small amounts of precipitated ferric hydroxide and Freundlich and Leonhardt (*Kolloid Chem. Beihefte*, 1915, **7**, 187) vanadium pentoxide and molybdenum trioxide by washing the precipitates with

water. Similarly, we could peptise congo-red coagulum simply by diluting with water when the sol is precipitated by monovalent cations (*Koll. Zeit.*, 1927, **43**, 389). Similar results were obtained by Ostwald (*Koll. Chem. Beihefte*, 1919, **10**, 226) with a sol of congo-rubin and by Ruer (*Z. anorg. Chem.*, 1905, **43**, 282) with zirconium hydroxide. In all these cases of peptisation by washing it is more difficult to peptise a precipitate by the coagulation of a sol by a polyvalent ion.

We have observed that a coagulum of antimonic acid can be peptised very easily when the sol is precipitated by monovalent ions but it becomes increasingly difficult to peptise the precipitate when the sol is coagulated by ions of higher valencies in the following manner:— The sol is precipitated by electrolytes at their precipitating concentrations and when the coagulum has settled 5 c.c. of the supernatant liquid are removed and then 5 c.c. of distilled water are added. If the coagulated mass is not obtained as a sol, the precipitate is again allowed to settle and the supernatant liquid is again removed and fresh water added. In the following table we shall record our results on the peptisation of the coagulum of antimonic acid sol by washing.

Electrolyte.	KCl	NaCl	NaOH	$BaCl_2$	$Al(NO_3)_3$
Number of washing.	2	2	1	6	8
Result.	A clear stable sol.	Do.	Do.	A turbid sol.	Do.

We have found that the precipitate obtained by coagulating the sol by monovalent cations appears to be smaller and less packed than that obtained by cations of higher valencies when they are examined under a microscope.

From the following experiment we have concluded that antimonic acid behaves as a reversible colloid:—20 C.c. of the sol were allowed to evaporate in a desiccator over concentrated sulphuric acid and an amorphous mass is left which immediately passes into a clear colloidal solution when it is made into a paste with cold distilled water and then diluted with water. It may be of interest to note that vanadium pentoxide, tungstic and molybdic acids also behave similarly. When, however, the solid residue of antimonic acid is strongly heated, it no more passes into a clear sol but a turbid suspension is obtained from which the oxide precipitates in the course of 24 hours. We have found that antimonic acid sol when air-dried leaves a hydrate of composition Sb_2O_5, $4{\cdot}7H_2O$. We

have observed that this hydrate of antimonic acid which forms a reversible colloid appreciably dissolves in water and together with the colloid some amount of antimonic acid is present as true solution. The amount dissolved is determined in the following manner:—50 C.c. of the colloid are coagulated with 10 c.c. *N*-KCl and to 50 c.c. of clear filtrate H_2S is passed, when antimony trisulphide and sulphur are precipiated. The mixture of Sb_2S_3 and sulphur are weighed in a Gooch crucible. 1·21 grams of Sb_2O_5, $4·7H_2O$ per litre of the colloid contain 0·0067 gram Sb_2O_5 in the dissolved condition which cannot be precipitated by KCl.

In an investigation on colloidal silicic, vanadic and tungstic acids we have observed that these sols when freshly prepared contain appreciable amounts of these substances in the dissolved condition, which gradually polymerises to the colloidal state, this change being most rapid in the case of silicic acid. We have shown that traces of alkali render these sols unstable whilst traces of acid stabilise them towards their coagulation by electrolytes because polymerisation is favoured by an acid, whilst alkali produces more simple molecules. In this paper we have, however, found that alkali possesses very little stabilising influence on antimonic acid sol. We are of opinion that this behaviour of antimonic acid results from the fact that the acid which is present in the molecular state does not polymerise so readily as in the cases of silicic, vanadic and tungstic acids.

Our view that antimonic acid is not polymerised markedly as is observed with silicic, vanadic and tungstic acids is supported by the fact that the change in the acidity, conductivity, and viscosity of antimonic acid with time is appreciably less than the change observed with any of the other sols. Thus antimonic acid possesses some properties akin to silicic, vanadic, tungstic and molybdic acids but they are developed to a lesser degree.

In a recent paper Chaudhuri (*Jour. Phys. Chem.*, 1928, **32**, 121) criticised our views on the influence of dilution of sols on their coagulation by electrolytes and has quoted certain extracts from a communication of Weiser on the same subject. In a previous publication (*J. Phys. Chem.*, 1927, **31**, 649), we have thoroughly met the points raised by Weiser and justified our views. In the same paper we have also shown that increase in the distance between colloid particles on diluting a sol cannot be the main cause of its stability towards monovalent electrolytes on dilution.

It is also apparent that the decreased chance of collision on diluting a sol will only affect the velocity of rapid coagulation but in our experiments as well as in the experiments of other workers, the coagulation is actually observed long after the addition of electrolytes when the decreased chance of collision is counteracted by the length of time. We have shown that when an ion carrying the same charge as the sol is not appreciably adsorbed, the dilution rule that the greater the concentration of the sol the greater is the amount of the electrolyte necessary for coagulation irrespective of the valency of the ion, is obeyed. This dilution rule has been found to be applicable to the following sols when coagulated by such electrolytes as yield similarly charged ions which do not possess marked chemical affinity for the sols:—

$Fe(OH)_3$ (positive and negative), $Cr(OH)_3$ (positive and negative), $Sn(OH)_4$ (positive and negative), $Ce(OH)_4$, WO_3, V_2O_5, gold, sulphur (Weimarn), $Zr(OH)_4$, antimony pentoxide, $Al(OH)_3$, $Th(OH)_4$ and MnO_2 (positive and negative). Compare *J. Phys. Chem.*, 1922, **26**, 701; 1924, **28**, 313; 1925, **29**, 435, 659; 1927, **31**, 187.

It must be emphasised that the influence of ions carrying the same charge as the sol is certainly specific and is only observable with some definite sols, when coagulated by electrolytes which yield a similarly charged ion capable of being adsorbed in appreciable amounts. We have shown that a sol of ferric hydroxide obeys the dilution rule when coagulated by electrolytes like KCl, K_2SO_4 etc., but behaves abnormally on dilution when coagulated by HCl, $FeCl_3$, $Al(NO_3)_3$ etc., because appreciable amounts of $H^{\cdot}$, $Fe^{\cdot\cdot\cdot}$ and $Al^{\cdot\cdot\cdot}$ ions are adsorbed by the positively charged sol. In this connection it will be interesting to note that Neidle (*J. Amer. Chem. Soc.*, 1917, **39**, 2334) showed that when increasing amounts of HCl are added to a pure sol of $Fe(OH)_3$ the stability of the sol goes on increasing up to a limiting value and increasing amounts of K_2SO_4 were necessary for coagulating the sol.

In a foregoing paper (*J. Phys. Chem.*, 1927, **31**, 187) we have shown that thorium hydroxide obeys the general dilution rule when coagulated by KCl, K_2SO_4 etc. and shows additive relationship when coagulated by mixtures of electrolytes. Very recently Desai (*Koll. Chem. Beihefte*, 1928, **26**, 357) has observed that this sol requires larger amounts of Cl ions when coagulated by a mixture of HCl and KCl. The results of Neidle and Desai are in support of our views expressed in *J. Phys. Chem.*, (1925, **29**, 435, 659).

The cataphoretic experiments of concentrated and diluted sols of As_2S_3 in presence of HCl by Mukherjee and Chaudhuri (*J. Chem. Soc.*, 1923, **123**, 213) also support our views. In a recent paper Chaudhuri (*J. Phys. Chem.*, 1928, **32**, 121) from his own experiments admits that adsorption of similarly charged ions plays an important part in the stability of certain sols towards their coagulation by monovalent ions.

Summary.

1. A negatively charged sol of antimony pentoxide has been obtained by dialysing a mixture of potassium antimonate and dilute nitric acid.

2. The sol follows the Schulze-Hardy law.

3. Antimonic acid sol behaves normally towards dilution, mixtures of electrolytes and does not show positive acclimatization and cannot appreciably adsorb similarly charged ions from electrolytes like KCl, $BaCl_2$, etc.

4. The viscosity, electric conductivity, acidity and stability towards electrolytes change slightly either on ageing or on boiling.

5. A coagulum of antimonic acid can be repeptised very easily by washing when the sol is precipitated by monovalent ions but with difficulty when coagulated by polyvalent ions.

6. It is a reversible colloid, and the hydrate Sb_2O_5, $4{\cdot}7H_2O$ obtained by drying the sol at the ordinary temperature passes into the colloidal state on the addition of water.

7. Experiments show that about 0·5% of the colloid is in the dissolved condition.

8. Antimonic acid sol possesses several properties similar to those of silicic, vanadic, tungstic and molybdic acids but these are less prominent with antimonic acid than in the cases of the other sols.

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On a New Series of Double Sulphates of the Copper-Magnesium Group and the Phosphonium Bases. Part I.

By Prafulla Chandra Ray and Nirmalendunath Ray.

In continuation of our work on double sulphates of the copper-magnesium group and the sulphonium bases (*J. Indian Chem. Soc.*, 1927, **4**, 37; 1928, **5**, 69) the present investigation has been undertaken.

As the tetraethylphosphonium hydroxide is as strong a base as the alkyl sulphonium hydroxides, as evidenced by their heats of neutralisation with sulphuric acid, it was expected that the sulphate of the former base would also yield a series of double salts with the vitriolic sulphates, *i.e.*, the sulphates of the copper-magnesium group. The expectation has been fully realised.

Although cobalt, nickel and zinc yield salts of the type $M''SO_4$, $[(C_2H_5)_4P]_2SO_4$, $8H_2O$ similar to salts of the trimethylsulphonium type (*loc. cit.*), *i.e.*, they yield octahydrated double salts, the behaviour of the magnesium and copper has been found to be somewhat anomalous in that the former yield salts not only of the usual type but also acid salts conforming to the following formulae:—

$2MgSO_4$, $[(C_2H_5)_4P]_2SO_4$, H_2SO_4.
$2MgSO_4$, $[(C_2H_5)_4P]_2SO_4$, $2H_2SO_4$, $2H_2O$.
$2MgSO_4$, $[(C_2H_5)_4P]_2SO_4$, H_2SO_4, H_2O.
$2MgSO_4$, $[(C_2H_5)_4P]_2SO_4$, H_2SO_4, $2H_2O$.

whereas copper yields only an acid salt of the type $2CuSO_4$, $[(C_2H_5)_4P]_2SO_4$, H_2SO_4, $4H_2O$.

In several preparations undertaken with magnesium, it has been found that the first few crops are acid salts and the subsequent crops are normal. This phenomenon seems to be due to the concentration of free acid evidently due to hydrolysis. As successive crops are collected a greater portion of the free acid in solution is taken up by the double sulphate molecule ; on further concentration

the tetraethylphosphonium hydroxide begins to decompose into $P(C_2H_5)_3$ and C_2H_5OH and hence the subsequent crops are neutral salts.

The properties of these double salts are very similar to those obtained from alkyl sulphonium sulphates and the vitriolic sulphates. The tetraethyl phosphonium double sulphates are crystalline, deliquescent substances, and are readily soluble in water. On heating on a platinum spatula they melt in the water of crystallisation and afterwards decompose, the organic component is found to burn on the spatula and the characteristic smell of alkyl phosphines is distinctly perceptible. These double sulphates have been found to be more stable than the triethyl sulphonium double sulphates.

On a review of the entire series of double sulphates with sulphonium and phosphonium bases, it will be noticed that in the case of the normal salts they are sometimes deca-hydrated and sometimes octa-hydrated. This is in marked contrast to the behaviour of the double sulphates of the copper-magnesium group with alkaline sulphates, *e.g.*, K_2SO_4, $(NH_4)_2SO_4$, etc., where they are invariably hexahydrated.

Experimental.

As in the case of the alkyl sulphonium sulphates, the tetraethyl phosphonium sulphate was prepared from the corresponding iodide. Preparation of a pure sample of the iodide* has been found to be a matter of great difficulty. The iodide was converted into the hydroxide by rubbing with excess of moist silver oxide in presence of water. The solution was filtered, the filtrate neutralised with dilute sulphuric acid and to this solution of tetraethyl phosphonium sulphate was added a solution of vitriolic sulphate, the amount of phosphonium sulphate being calculated from the amount of the iodide taken. Now, an excess of phosphonium iodide has always to be used as in the cases of alkyl sulphonium double salts (*loc. cit.*), the reason being that a considerable portion of the iodide is lost in the form of an insoluble double salt with silver iodide. The solution containing the organic and inorganic sulphates was concentrated at first in a vacuum over sulphuric acid and finally left to spontaneous evaporation.

* An account of the preparation of pure tetraethyl phosphonium iodide has been given in a previous paper recently communicated to the Society (this *Journal*, 1928, 6, 733).

During crystallisation the mother-liquor assumed a thick syrupy state. The crystals of the double sulphates were drained free from the mother-liquor and dried between folds of filter paper.

In the case of the normal salts successive crops of the same preparation were collected and on analysis were found to be of identical composition.

A difficulty was encountered with the two acid salts of magnesium, *viz.*,

$$2MgSO_4\ [(C_2H_5)_4P]_2SO_4,\ H_2SO_4,\ H_2O$$

and $2MgSO_4,\ [(C_2H_5)_4P]_2SO_4,\ H_2SO_4,\ 2H_2O.$

It will be noticed that there is only a difference of a molecule of water of crystallisation. Otherwise the two salts are identical. As only analytical results were taken into account for the determination of the number of water molecules, and as the salts are hygroscopic, it is difficult to say whether they are hydrated or not.

Cobalt tetraethyl phosphonium sulphate.—The first crop consisted of pure cobalt sulphate ; the second crop of the double sulphate contained traces of cobalt sulphate; but the third and successive crops consisted of the pure double sulphate. This is due to the fact that the cobalt sulphate itself is less soluble than the double sulphate. A similar behaviour was noticed in the case of the double sulphates of cobalt with ethyl sulphonium sulphate (*J. Indian Chem. Soc.*, 1928, **5**, 70).

This double salt was coloured like cobalt sulphate crystals.

(Found : Co, 8·3, 8·45 ; SO_4, 27·89, 27·75 ; C,*26·90 ; H, 8·01. $CoSO_4,\ [(C_2H_5)_4P]_2SO_4,\ 8H_2O$ requires Co, 8·56 ; SO_4, 27·87 ; C, 27·87 ; H, 8·13 per cent.)

Zinc tetraethyl phosphonium sulphate.—It was obtained as a white crystalline compound. (Found: Zn, 9·26 ; SO_4, 26·78. $ZnSO_4[(C_2H_5)_4P]_2SO_4,\ 8H_2O$ requires Zn, 9·35 ; SO_4, 27·62 per cent.)

Nickel tetraethyl phosphonium sulphate was a crystalline substance coloured like nickel sulphate. (Found: Ni, 8·31, 8·72 ; SO_4, 27·61 ; H, 8·01. $NiSO_4[(C_2H_5)_4P]_2\ SO_4,\ 8\ H_2O$ requires Ni, 8·51 ; SO_4, 27·86 ; H, 8·12 per cent).

* The carbon generally comes out too low. This is probably due to the fact that traces of PEt_3 formed by decomposition readily escape oxidation.

Magnesium tetraethyl phosphonium sulphates.—All the double salts with magnesium were obtained in colourless transparent crystals.

The normal salt.—

(Found: Mg, 3·63, 3·67 ; SO_4, 28·44. $MgSO_4[(C_2H_5)_4P]_2SO_4$, $8H_2O$ requires Mg, 3·67 ; SO_4, 29·51 per cent.)

The acid salts.—

(*a*) $2\,MgSO_4\ [(C_2H_5)_4P]_2SO_4,\ H_2SO_4$:—(Found: Mg, 6·55 ; SO_4, 52·72. Theory requires Mg, 6·60 ; SO_4, 52·74 per cent.)

(*b*) $2MgSO_4\ [(C_2H_5)_4P]_2SO_4,\ 2H_2SO_4, 2H_2O$:—(Found: Mg, 5·53 ; SO_4, 56·45. Theory requires Mg, 5·57 ; SO_4, 55·69 per cent.)

This salt on recrystallisation gives $2MgSO_4,\ [(C_2H_5)_4P]_2SO_4,\ H_2SO_4$ (see above).

$2MgSO_4\ [(C_2H_5)_4P]_2SO_4,\ H_2SO_4,\ H_2O$:—

(Found: Mg, 6·33 ; SO_4, 51·90. Theory requires Mg, 6·43 ; SO_4, 51·47 per cent.)

$2MgSO_4\ [(C_2H_5)_4P]_2SO_4,\ H_2SO_4,\ 2H_2O$:—

(Found: Mg, 6·08 ; SO_4, 50·32. Theory requires Mg, 6·28 ; SO_4, 50·26 per cent.)

Copper tetraethyl phosphonium sulphate —This substance was obtained as a light blue crystalline compound. (Found: Cu, 14·08, 14·32 ; SO_4, 41·83, 41·87. $2\,CuSO_4\ [(C_2H_5)_4P]_2SO_4,\ H_2SO_4,\ 4H_2O$ requires Cu, 14·35 ; SO_4, 43·70 per cent.)

In conclusion we beg to express our sincere thanks to Mr. K. C Bose-Rây for his ungrudging help in conducting some of the experimental work in connection with the investigation.

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The Change of Precipitating Concentrations of Electrolytes with the Purity and Temperature of Some Hydroxide Sols.

By N. R. Dhar and V. Gore.

In publications from these laboratories (*Zeit. anorg. Chem.*, 1927, **162**, 237 ; **168**, 209 ; *Koll. Zeit.*, 1927, **42**, 120) we have shown that the viscosity and the stability of hydrophobe colloids decrease on ageing, and those of hydrophile colloids increase with time up to a limiting value. The electric conductivity and the surface tension become greater with hydrophobe colloids and less with hydrophilic colloids with time. It will be evident therefore, that the composition and constitution of colloids constantly change with time. We have also shown that this change of properties and hence of composition of a colloid is more pronounced with sols prepared in the cold than at high temperatures. This is due to the fact that the adsorptive capacity of the particles of a hydrophobe colloid becomes less with time and hence the adsorbed electrolyte is given out. This process is facilitated by increasing the temperature of a colloid.

We have emphasised that as the colloid has no definite composition and it changes with time, the determination of the constitution by Pauli and co-workers (*Koll. Zeit.*, 1917, **21**, 49 ; *Z. physikal. Chem.*, 1927, **129**, 199), Zsigmondy (*Z. Physikal. Chem.*, 1922, **101**, 292 ; 1926, **124**, 145), Wintgen (*Z. Physikal. Chem.*, 1923, **103**, 238 ; 1924, **109**, 378) and others loses much of its significance. It appears also that research in colloid chemistry has not been systematic because each experimenter prepared the sol in his own particular manner, and the colloid contained different impurities and hence the stability and other properties are likely to vary from one specimen to another of the same sol prepared in different ways.

Recently we have shown if N_1, N_2, N_3,.....N_x be the precipitating concentrations of uni-, bi-, tri-... x-valent ions, then

$$N_1 : N_2 : N_3 \ldots\ldots : N_x = 1 : \tfrac{1}{2}\alpha : \tfrac{1}{3}\alpha^2 \ldots\ldots \frac{1}{x}\alpha^{x-1}, \quad \text{where } \alpha = e^{\frac{-qe}{Dr}/kT}$$

i.e. α lies between 0 and 1 and is a proper fraction q = charge on

a colloid; D=dielectric constant of the medium; r=distance of the double layer; k=Boltzmann constant; T=absolute temperature).

It follows from the foregoing relation that when q decreases or T increases, a tends to become unity. In other words, as the charge on the colloid particles decreases the precipitating concentration of uni-, bi- and tri-valent ions tend to be in the ratio 1 : $\frac{1}{2}$: $\frac{1}{3}$.

Moreover when the temperature becomes high there should be a tendency of the precipitating concentrations to arrange in the above manner.

In actual practice the foregoing relation cannot be realised because the sol is likely to coagulate when the charge becomes zero. But we should observe that the ratio of the precipitating concentrations of ions of different valencies should decrease as the charge on the colloid particles decreases it is well known that the stability of a sol decreases with increasing purity.

In this communication we have prepared sols of ferric hydroxide, chromic hydroxide and zirconium hydroxide of different degrees of purity and have shown that the ratio of the precipitating concentrations of uni-, bi- and tri-valent ions decreases considerably as the purity of the sol is increased.

We have also shown that the ratio of the precipitation concentrations of uni- and bi-valent ions on sols of stannic hydroxide, zirconium hydroxide and ceric hydroxide decreases as the temperature of coagulation is increased.

Ferric hydroxide sols.

A solution of Kahlbaum's ferric chloride was added to boiling water and a clear brownish red sol was obtained. This sol was put in a parchment paper bag and was dialysed in hot water (80°-90°). The water in the dialysis was changed from time to time.

The dialysis was continued for 8 to 9 days and the amount of silver chloride obtained by adding silver nitrate to the sol dissolved in nitric acid became less and less with progressive dialysis.

After 8 or 9 days' dialysis the amount of silver chloride obtainable becomes small and when the hot dialysis is pushed still further invariably the sol coagulates to a red gelatinous precipitate of ferric hydroxide.

A sol of ferric hydroxide containing 2·86 gms. of Fe_2O_3 per litre and 0·0324 gm. Cl per litre was obtained by hot dialysis for 6 days

but on keeping in a stoppered Jena glass bottle it coagulated to a brownish red gelatinous precipitate after 30 hours. The filtrate after the separation of the precipitate showed very slight test for Cl, while the precipitate when dissolved in nitric acid gave a slightly greater amount of Cl.

As the dialysis progressed from time to time 150 c.c. of the sol were taken out and its iron content determined by evaporating 10 c.c. of the sol and igniting in a platinum crucible. The chlorine content was determined by adding pure strong nitric acid to 20 c.c. of the sol, the precipitate of ferric hydroxide which first appeared dissolved when the mixture was warmed and the chlorine ion was precipitated as silver chloride. The ratio of the weight of the ferric hydroxide to the weight of chlorine per litre was a measure of the purity of the sol. The sol was coagulated by chloride, sulphate and citrate of potassium.

Ferric hydroxide sols.

(1) After two day's hot dialysis.

Concentration of the sol = 3·5 gms. Fe_2O_3 per litre.

Amount of Cl = 1·623 gms. per litre.

Fe_2O_3/Cl = 2·1; Volume = 5 c.c.; Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate in c.c.	Amount of K_2SO_4 to coagulate in c.c.	Mono/bi.
1 c.c.	2·3 c.c. of 2 N	1·4 c.c. of N/200	657·1

(2) After four days' hot dialysis.

Concentration of the sol = 5·76 gms. Fe_2O_3 per litre.

Amount of Cl = 0·2926 gms. ,, ,,

Fe_2O_3/Cl = 19; Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate in c.c.	Amount of K_2SO_4 to coagulate in c.c.	Mono/bi.
0·5 c.c.	0·3 c.c. of N	0·6 c.c. of N/400	200·0
1·0 c.c.	0·4 c.c. of N	0·8 c.c. of N/400	200·0

(3) After seven day's hot dialysis.

Concentration of the sol = 11·24 gms. Fe_2O_3 per litre.

Amount of Cl = 0·3749 gms. ,, ,,

Fe_2O_3/Cl = 29; Volume = 5 c.c.; Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate in c.c.	Amount of K_2SO_4 to coagulate in c.c.	Mono/bi.
0·5 c.c.	1·1 c.c. of N/20	0·7 c.c. N/400	31·4
1·0 c.c.	1·2 c.c. of N/20	0·8 c.c. N/400	30·0

(4) After ten days' hot dialysis.

Concentration of the sol = 7·7 gms. Fe_2O_3 per litre.

Amount of Cl = 0·0936 gms. ,, ,,

Fe_2O_3/Cl = 82·2; Volume = 5 c.c.; Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate in c.c.	Amount of K_2SO_4 to coagulate in c.c.	Mono/bi.
2 c.c.	0·35 c.c. of N/50	0·3 c.c. of N/400	8·8
4 c.c.	0·30 c.c. of N/50	0·3 c.c. of N/400	8·0

Ferric hydroxide sols (new preparations).

(5) After 6 days' hot dialysis.

Concentration of the sol = 4·42 gms. Fe_2O_3 per litre

Amount of Cl = 0·1768 grms. ,, ,,

Fe_2O_3/Cl = 25 ; Volume = 5 c.c ; Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	Amount of K-citrate to coagulate.	Mono. Bi	Mono. Tri
1 c.c.	2 c.c. N/20	0·4 c.c. N/200	1·5 c.c. of N/1000	50	66·6

(6) After 8 days' hot dialysis.

Concentration of the sol = 3·72 gms. Fe_2O_3 per litre.

Amount of Cl = 0·05727 gms. ,, ,,

Fe_2O_3/Cl = 64·9; Volume = 5 c.c. ; Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	Amount of K-citrate to coagulate.	Mono. Bi	Mono Tri
1 c.c.	0·7 c.c. N/20	0·5 c.c. N/400	1 c.c. N/1000	28	35

Chromium Hydroxide Sols.

The procedure with this sol was the same as in the case of ferric hydroxide, the starting material in this case being Kahlbaum's trichloride of chromium.

(1) After 5 days' hot dialysis.

Concentration of the sol = 0·86 gms. Cr_2O_3 per litre
Amount of Cl = 0·1332 gm. ,, ,,
Cr_2O_3/Cl = 6·53. Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	$\frac{\text{Mono}}{\text{Bi}}$.
1 c.c.	> 4 c.c. of 4N	1·3 c.c. of N/200	>2400

(2) After 7 days' hot dialysis.

Concentration of the sol = 0·98 gms. Cr_2O_3 per litre
Amount of Cl = 0·06847 gms. ,, ,,
Cr_2O_3/Cl = 14·3. Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	$\frac{\text{Mono}}{\text{Bi}}$.
1 c.c.	1·7 c.c. of 4N	1 c.c. N/200	1360
2 c.c.	1·8 c.c. of 4N	1·1 c.c. N/200	1309

(3) After 10 days' hot dialysis.

Concentration of the sol = 0·98 gms. Cr_2O_3 per litre
Amount of Cl = 0·05602 gms. ,, ,,
Cr_2O_3/Cl = 17·4. Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	Amount of K-citrate to coagulate.	$\frac{\text{Mono}}{\text{Bi}}$.	$\frac{\text{Mono}}{\text{Tri}}$.
0·5 c.c.	0·8 c.c. 4N	0·7 c.c. N/200	...	914·2	...
1·0 c.c.	0·9 c.c. 4N	0·9 c.c. N/1000	2·3 c.c. N/1000	800·0	1565·2
2·0 c.c.	0·9 c.c. 4N	1·1 c.c. N/200	...	645·5	...

(4) After 17 days' hot dialysis.

Concentration of the sol = 1·76 gms. Cr_2O_3 per litre
Amount of Cl = 0·04897 gms. ,, ,,
Cr_2O_3/Cl = 35·9. Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	Amount of K-citrate to coagulate.	$\frac{\text{Mono}}{\text{Bi}}$.	$\frac{\text{Mono}}{\text{Tri}}$.
1 c.c.	2 c.c. of N/50	0·4 c.c. N/200	1 c.c. of N/1000	90	40

(5) After 18 days' hot dialysis.

Concentration of the sol = 2·02 gms. Cr_2O_3 per litre.

Amount of Cl = 0·01692 gms. ,, ,,

Cr_2O_3/Cl = 119·3. Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	Amount of K-citrate to coagulate.	Mono / Bi	Mono / Tri
1 c.c.	0·3 c.c. of N/20	0·3 c.c. of N/200	0·7 c.c. of N/1000	10	21·4

(6) After 20 days' hot dialysis.

Concentration of the sol = 2·02 gms. Cr_2O_3 per litre.

Amount of Cl = 0·01618 gms. ,, ,,

Cr_2O_3/Cl = 124·8.

No measurements could be made with the chromium hydroxide sol No. (6), as it coagulated by itself. Hence the sol becomes highly unstable when the ratio Cr_2O_3/Cl is greater than 120. It appears, therefore, that the statement of Neidle and Barab (*J. Amer. Chem. Soc.*, 1916, **38**, 1961) that the ratio in their sol was above 1500 needs confirmation.

In publications from these laboratories we have shown theoretically and experimentally that the viscosity of sols decreases as the charge increases (*Zeit. Elektrochem.*, 1925, **31**, 261; *J. Phys. Chem.*, 1925, **29**, 1556 ; 1926, **30**, 1616 ; *Zeit. anorg. Chem.*, 1926, **152**, 393 ; *Koll. Zeit.*, 1927, **42**, 124 ; 1928, **44** 225). Chakravarti and Dhar measured the viscosity of a sol of chromium hydroxide containing 3·135 gms. Cr_2O_3 per litre and the value was 0·01079 at 23·1° (water = 0·00937). This sol was dialysed for a fortnight in the cold. We have now measured the viscosity of the highly purified sol No. 5 and find that its viscosity (0·02911 at 30°; water at 30° = 0·00803) is much higher than that obtained with the sol which has not been so highly purified. Hence it appears that as the charge on a sol decreases, the viscosity markedly increases. Exactly similar results have been obtained with ferric hydroxide sols.

Zirconium Hydroxide Sols.

The material from which the sol was prepared was Kahlbaum's zirconium oxychloride and the procedure was the same as in the previous cases.

(1) After 2 days' hot dialysis.

Concentration of the sol = 9·12 gms. ZrO_2 per litre.

Amount of Cl = 2·2397 gms. per litre

ZrO_2/Cl = 4·7. Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	$\frac{\text{Mono}}{\text{Bi}}$.
1 c.c.	>4 c.c. of 4N	0·26 c.c. of N/5	>308

(2) After 4 days' hot dialysis.

Concentration of the sol = 4·48 gms. ZrO_2 per litre.

Amount of Cl = 1·2985 gms. ,, ,,

ZrO_2/Cl = 7·3. Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	Amount of K-citrate to coagulate.	$\frac{\text{Mono}}{\text{Bi}}$.	$\frac{\text{Mono}}{\text{Tri}}$.
1 c.c.	1·1 c.c. of 4N	0·7 c.c. of N/20	2·2 c.c. N/50	125·7	100

(3) After 7 days' hot dialysis,

Concentration of the sol = 5·2 gms. ZrO_2 per litre

Amount of Cl = 0·559 gms ,, ,,

ZrO_2/Cl = 9·3. Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	Amount of K-citrate to coagulate.	$\frac{\text{Mono}}{\text{Bi}}$.	$\frac{\text{Mono}}{\text{Tri}}$.
1·0 c.c.	0·7 c.c. of 2N	2·8 c.c. of N/200	0·8 c.c. of N/50	100·0	88·5

(4) After 12 days' hot dialysis.

Concentration of the sol = 2·14 gms. ZrO_2 per litre

Amount of Cl = 0·1942 gms. ,, ,,

ZrO_2/Cl = 11·1. Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	$\frac{\text{Mono}}{\text{Bi}}$.
1 c.c.	0·55 c.c. of N	1·2 c.c. of N/200	91·0

The sols employed so far were perfectly clear in both reflected and transmitted light and their acid content was only hydrochloric.

Some experiments are carried on with a sol of ferric hydroxide prepared in the following manner. Freshly obtained ferric hydroxide prepared in the cold was freed from chloride ion and was peptised to

a turbid sol with a minimum quantity of ferric chloride. A part of the sol th is obtained was boiled for half an hour and was dialysed in the cold. The other portion of the sol which was not boiled was also dialysed. The dialysis was continued for three weeks and the iron and chlorine contents were determined. The sols were coagulated by KCl and K_2SO_4 and the following results were obtained. Both these sols were very unstable and partly coagulated on dilution with water.

Boiled sol of ferric hydroxide.

Concentration of the sol = 4·4 gms. Fe_2O_3 per litre.

Amount of Cl = 0·02365 gms. ,, ,,

Fe_2O_3/Cl = 186. Volume = 5 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	$\frac{\text{Mono}}{\text{Bi}}$
4 c.c.	0·7 c.c. N/100.	0·3 c.c. N/4	9·8.

Unboiled sol of ferric hydroxide.

Concentration of the sol = 4·94 gms. Fe_2O_3 per litre.

Amount of Cl = 0·04108 gms. per litre.

Fe_2O_3/Cl = 120. Volume = 10 c.c. Time = 1 hour.

Amount of sol.	Amount of KCl to coagulate.	Amount of K_2SO_4 to coagulate.	$\frac{\text{Mono}}{\text{Bi}}$
1 c.c.	1·1 c.c. of N/100	0·5 c.c. of N/400	8·1
4 c.c.	0·7 c.c. of N/50	0·7 c.c. of N/400	8·0

Hence the results show that when the sol is very pure and unstable, the ratio of the precipitating concentrations of mono- and bi-valent becomes as small as 8.

The experimental results show that the ratio of the precipitating concentrations of mono- bi- and tri-valent ions decreases considerably as the ratio of the Fe_2O_3 to Cl increases. A similar behaviour is observed with the other sols. As the purity of the sol increases the electric charge on the particles decreases. The amounts of the electrolyte necessary for coagulation become less but the ratio of the precipitating concentrations of mono- and bi-, and mono- and tri-valent ions considerably decreases with the purity. These experimental results support the theoretical deduction already stated.

In several publications from these laboratories (*J. Phys. Chem.*, 1925, **29**, 435, 659; 1927, **31**, 649) we have shown with different types of sols that the precipitating concentrations of uni-, bi- and tri-valent ions are very seldom in the ratio $1 : x : x^2 \ldots$ as demanded by Whetham's rule (*Phil. Mag.*, 1894, **48**, (*v*), 474). On surveying the literature on coagulation it could be easily seen that the ratios of the precipitating concentrations are always smaller in the case of those sols which can be obtained readily in a more or less pure state than in the case of those which are usually associated with large quantities of peptising or other electrolytes.

The difference in the coagulating powers of different ions towards one and the same sol prepared by different investigators is mainly due to the difference in the impurities and peptising agents retained by the sols.

In this connection it will be worth while remarking that the sulphide sols and specially arsenious sulphide is a very unsatisfactory substance for the investigation of the physical and chemical properties of a colloid, because the sol cannot be completely freed from either an excess of H_2S or arsenious acid and on keeping even in the dark the electric conductivity appreciably increases and on exposure to light the electric conductivity greatly increases (compare Ghosh and Dhar, *Koll. Zeit.*, 1925, **36**, 129). Along with the change in the electric conductivity, change in the composition and physical properties is also observed. Hence accurate work can be satisfactorily carried on with specially purified sols of ferric hydroxide, chromic hydroxide, zirconium hydroxide, gold, etc., which can be obtained in a fairly pure condition more readily and their composition changes much less readily than the arsenious sulphide, mastic and other sols, which are hydrolysed.

In order to investigate the influence of temperature on the ratio of the precipitating concentrations some experiments have been carried on the coagulation of sols of stannic hydroxide, zirconium hydroxide and ceric hydroxide. The results are as follows.

Stannic Hydroxide Sol.

Stannic hydroxide was precipitated by the action of an excess of ammonium hydroxide on stannic chloride solution. The precipitate on washing once or twice with water passes into negatively charged clear sol, which was purified by dialysis.

Concentration of the sol = 6·66 gms. of SnO_2 per litre.

Amount of sol taken each time = 1 c.c.

Total volume = 10 c.c. Time = 1 hour.

Electrolyte.	Amount to coagulate in c.c.			
	At 30°.		At 60°.	
Potassium chloride N/4	2·4	109	1·4	82
Barium chloride N/200	1·1		0·85	

Zirconium Hydroxide Sol.

A solution of zirconium nitrate was boiled vigorously for half an hour and was dialysed for 10 days and a clear sol was obtained.

Concentration of the sol = 9·36 gms. of ZrO_2 per litre.

Amount of sol taken each time = 2 c.c.

Total volume = 10 c.c. Time = 1 hour.

Electrolyte.	Amount to coagulate in c.c.			
	At 30°.		At 60°.	
KCl N/4	1·1	29	0·4	13
$BaCl_2$ N/200	1·9		1·55	

Ceric Hydroxide Sol.

25 Gms. of ceric-ammonium nitrate were dissolved in 250 c.c. of water at 25°. The solution was dialysed for 6 days after filtering.

Concentration of the sol = 17·65 gms. of CeO_2 per litre.

Volume of the mixture = 10 c.c.

Amount of sol taken each time = 1 c.c. Time = 1 hour.

Electrolyte.	Amount to coagulate in c.c.			
	At 30°.		At 60°.	
KCl N/4	4·8	171	2·1	75
K_2SO_4 N/200	1·4		1·4	

The above results show that as the temperature is increased the ratio of the precipitating concentrations of uni- and bi-valent ions on the coagulation of these sols decreases. These results are in the support of the theoretical deduction already discussed where it is predicted that as the temperature increases, the value of α tends to

become unity and $N_1 : N_2 : N_3 = 1 : \frac{1}{2} : \frac{1}{3}$. It appears that as the temperature is increased the amount of adsorbed electrolyte retained by the sol decreases due to the decrease in the surface and activity of the colloid particles and consequently the sols are expected to be less stable and would require smaller amount of electrolytes than when coagulated at low temperatures. This relation will not be observed with those sols which are hydrolysed, *e.g.*, mastic, arsenious sulphide, gum dammar, Prussian blue, etc. With these sols increase of temperature will lead to increased hydrolysis and stability. (compare Ghosh and Dhar, *J. Phys. Chem.*, 1925, **29**, 659; 1926, **30**, 830; *Koll. Zeit.*, 1926, **38**, 141; 1926, **39**, 346).

It is well known that the amount of univalent ions necessary for coagulation is much greater than that of polyvalent ions. Consequently a slight change in the amount of adsorption of the peptising electrolyte and hence the purity of the sol will affect the coagulating power of a monovalent ion more markedly than that of a polyvalent ion. By increase of temperature the adsorbed electrolyte becomes less and the charge decreases and hence the decrease in the amount of univalent ion required for coagulation is more pronounced than that with polyvalent ions and thus the ratio of the precipitating concentrations of uni- and poly-valent ions will decrease with increase of temperature.

Experimental results obtained in this laboratory show that the ratio of the precipitating concentrations of uni- and bi-valent ions is smaller in the case of sols which have been exposed to light than in the case of sols kept in the dark.

With progressive hot dialysis the same behaviour is also expected and the amount of free and adsorbed electrolyte decreases and the decrease in the amount of univalent ions necessary for coagulation is more marked than the decrease in the amount of a polyvalent ion required for coagulation.

These conclusions are strongly supported by the following measurements of Ghosh and Dhar (*J. Phys. Chem.*, 1927, **31**, 649) on the coagulation of ferric sol by mixtures of HCl and KCl and HCl and K_2SO_4.

Concentration of the sol = 1·43 gms. Fe_2O_3 per litre.

Amount of sol taken each time = 2 c.c.

Volume = 6 c.c. Immediate turbidity is observed.

HCl N/100 added in c.c.	0	0·1	3·3	0·5	0·7	0·9
KCl to coagulate in c.c.	0·95 of N/5	0·85 of N	1·55 N	1·85 N	1·05 N	1·95 N

Coagulation with K_2SO_4 *in presence of* HCl.

N/100 HCl added in c.c.	0	0·2	0·5	0·7	0·9
N/400 K_2SO_4 to coagulate in c.c.	0·56	0·95	1·05	1·10	1·10

Hence in presence of small quantities of HCl, the precipitating concentration of KCl is enormously increased whilst that of K_2SO_4 is increased slightly.

The foregoing results show that the view held by a number of investigators that the dialysed ferric hydroxide colloid is really an oxychloride cannot be held. Neidle (*J. Amer. Chem. Soc.*, 1917, **39**, 2334) believes that the oxychloride with 21 as the ratio of iron to chlorine in equivalents exists in colloidal ferric hydroxide. Recently Thomas and Frieden (*ibid*, 1923, **45**, 2522) have arrived at the conclusion that one mol. of ferric chloride is necessary to keep 21 mols. of ferric oxide dispersed in the colloidal condition irrespective of the concentration of the sol. Our results are not in agreement with these conclusions.

Bradfield (*ibid*, 1920, **44**, 965) prepared a ferric hydroxide sol by washing with the use of centrifuge in which the ratio was 396; the sol that we prepared starting from ferric hydroxide and dialysing in the cold gave a ratio of 180 and this was very unstable. It appears that Bradfield's sol must have been extremely unstable. The statement of Ufer (*Dissertation*, Dresden, 1915) that the ratio in his sol prepared by dialysis was 2700 and the recent report of Sorum (*J. Amer. Chem. Soc.*, 1928, **50**, 1263) that the ratio of his sol obtained by hot dialysis must have been greater than 14000 appears doubtful because even with extreme care our sols of ferric hydroxide prepared by hot dialysis coagulated by themselves when the ratio of Fe_2O_3 to Cl became about 90.

Summary.

(1) Sols of ferric hydroxide, chromium hydroxide and zirconium hydroxide of different degrees of purity have been prepared by hot dialysis starting from the chloride of the respective metals and the ratios of the precipitation concentrations of uni- and bi- and uni- and tri-valent ions have been determined.

(2) The ratio of the amount of the oxide of the metal and the chloride content is a measure of the purity of the sol.

(3) The ratio of the precipitation concentrations of uni- and bivalent ions has also been measured with highly purified sols of ferric hydroxide obtained from precipitated ferric hydroxide and peptised

by ferric chloride and purified by long dialysis at the ordinary temperature.

(4) In all cases the ratios of the precipitation concentrations of uni- and bi-valent and uni- and tri-valent ions markedly decrease as the purity and the ratios of the oxide of the metal and the chloride content increase.

(5) The viscosity of a sol increases with its purity even when its concentration is constant.

(6) The ratios of the precipitation concentrations of uni- and bi-valent ions have been measured with sols of stannic, zirconium and ceric hydroxides at 30° and 60°. The ratios are smaller at 60° than at 30°.

(7) As the charge on a colloid decreases or the temperature is increased the ratios of the precipitation concentrations of uni- and bi-valent and uni- and tri-valent ions decrease and the precipitating concentrations of uni-, bi-, and tri-valent ions tend to be in the ratio $1 : \frac{1}{2} : \frac{1}{3}$ in the case of sols which are not hydrolysed. This relationship has also been obtained theoretically.

(8) The precipitating concentrations of uni-, bi- and tri-valent ions are very seldom in the ratio $1 : x : x^2$ as demanded by Whetham's rule.

(9) The ratios of the precipitating concentrations are always smaller in the cases of those sols which can be obtained readily in the pure state than in the cases of sols, which are usually associated with large quantities of peptising electrolytes.

(10) Experimental results show that the ratio of the precipitating concentrations of uni- and bi-valent ions is smaller in the case of sols which have been exposed to light than in the case of sols kept in the dark.

(11) In presence of smaller quantities of hydrochloric acid, the precipitating concentration of potassium chloride is enormously increased, whilst that of potassium sulphate is increased slightly.

(12) The difference in the coagulating powers of different ions towards the same sol prepared by different investigators is mainly due to the difference in the peptising agents retained by the sols. This difference is more marked in the precipitating concentrations of univalent ions than with polyvalent ones.

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Kinetic Salt Effect. Part II. Velocity of Ionic Reactions at Great Dilutions.

By A. N. Kappanna.

Excluding the recent work of Brönsted and Livingston (*J. Amer. Chem. Soc.*, 1927, **49**, 435) on the velocities of reaction between bromopentammine cobaltic and hydroxyl ions and bromopentammine cobaltic and mercuric ions, so far as the author is aware, there seems to be no other work on record relative to the measurement of velocities of ionic reactions at very great dilutions. These authors found that activity coefficients for ions calculated on the basis of Debye's limitation equation, accurately predict the courses of the two reactions with change in total ionic strength.

The classical equation for the velocity of a bimolecular reaction is

$$-\frac{dx}{dt} = K\, C_A C_B$$

Brönsted's equation is $$-\frac{dx}{dt} = K_1 C_A C_B \frac{f_A f_B}{f_x}$$

Therefore $$K = K_1 \frac{f_A f_B}{f_x} \qquad \ldots (1)$$

From this it is clear that K varies as $\frac{f_A f_B}{f_x}$. Employing Debye's equation for the activity coefficient of an ion,

$$-\log f = 0{\cdot}50 Z^2 \sqrt{\mu}$$

where Z is the valence of the ion concerned, μ the ionic strength and 0·5, a factor whose value varies slightly with temperature (0·50 being the value in the neighbourhood of 20°C.)

$$-\log \frac{f_A \cdot f_B}{f_x} = \sqrt{\mu}\, 0{\cdot}50 \left[Z_A^2 + Z_B^2 - (Z_A + Z_B)^2 \right]$$

$$= -Z_A Z_B \sqrt{\mu} \qquad \ldots (2)$$

This expression shows that if Z_A and Z_B are of the same sign, the activity factor will be positive, and negative if they are dissimilarly charged. From (1) and (2) we get

$$\log K = \log K_1 + Z_A Z_B \sqrt{\mu} \quad \ldots \quad (3)$$

This equation provides a method for testing the validity of Debye's equation on the basis of Brönsted's theory, provided we work below a concentration of about $0{\cdot}01\mu$.

The mode of reaction between ions in solution can be visualised, as has been done by Soper (*J. Phys. Chem.*, 1927, **31**, 1790 and *J. Chem. Soc.*, 1928, **133**, 1235) from yet another standpoint. Soper starts with the assumption that the energy of activation is sensibly constant in aqueous solutions and is made up of energy given by a Maxwell distribution and of a potential energy possessed by reacting ions due to their electrical charges. If E_K represents the total kinetic energy of the two reacting ions and E_P their potential energy the velocity expression may be written in the form

$$-\frac{dx}{dt} = K_1 \, C_A . \, C_B . \, e^{-E_K + E_P/RT} \quad \ldots \quad (4)$$

as compared with the classical equation

$$-\frac{dx}{dt} = K \, C_A C_B .$$

From these two equations we get

$$K = K_1 \, e^{-E_K + E_P/RT} \quad \ldots \quad (5)$$

The potential energy due to the electrical field when calculated from the standpoint of Debye-Huckel theory and substituted in equation (5) gives the relation

$$\log K = \left[\log K_1 - \frac{E_K}{RT} \right] + Z_A Z_B \sqrt{\mu}$$

$$= \text{Constant} + Z_A Z_B \sqrt{\mu} \quad \ldots \quad (6)$$

It is rather interesting to find that equations (3) and (6), which have been derived from quite different standpoints, are absolutely identical with one another.

Independently of Brönsted's theory therefore Soper's theory provides us a method of testing Debye-Huckel equation for the activity coefficient of an ion.

It was the purpose of the present investigation to study the kinetics of the reaction described in a previous paper (*J. Indian Chem. Soc.*, 1928, **5**, 293), at very great dilution to test the validity of equation (3) or (6).

Preliminary experiments showed that even at 50°, velocity of reaction at great dilutions becomes extremely slow, but that monobromacetate reacts with thiosulphate at fairly measurable rates at great dilutions even at 30°. This latter reaction has accordingly been studied.

Experimental.

The reaction was followed by titrating known volumes of the reaction mixture with N/100-iodine solution, standardised carefully before each day's work. Velocity measurements were made at 30°, 40° and 50° between total ionic concentrations 0·0025 and 0·10 μ.

Tables I—VII give the results of a few experiments at 30°.

Table I.

$CH_2Br\ COONa = 0{\cdot}001$ M; $Na_2S_2O_3 = 0{\cdot}0005$ M

Ionic concentration = 0·0025 μ; 100 c.c. titrated.

Time in min.	C.c. $Na_2S_2O_3$.	C.c. bromacetate.	K.
0	4·90	9·90	—
150	4·60	9·60	0·1880
350	4·20	9·20	0·2000
540	3·90	8·90	0·1960
960	3·30	8·30	0·1992
1,470	2·75	7·75	0·1996
		Mean	0·1960

Table II.

$CH_2Br\ COONa = 0{\cdot}002$ M; $Na_2S_2O_3 = 0{\cdot}00$ M

Ionic concentration = 0·005 μ; 50 c.c. titrated.

Time in min.	C.c. $Na_2S_2O_3$.	C.c. bromacetate.	K.
0	4·95	9·95	—
180	4·20	9·20	0·208
400	3·45	8·45	0·215
600	2·90	7·90	0·219
1,320	1·75	6·75	0·214
		Mean.	0·214

TABLE III.

$CH_2Br\ COONa = 0{\cdot}001$ M; $Na_2S_2O_3 = 0{\cdot}002$ M ;

Ionic concentration $= 0{\cdot}007\ \mu$; 50 c.c. titrated.

Time in min.	C.c. $Na_2S_2O_3$	C.c. bromacetate.	K
0	9·75	4·75	—
180	9·00	4·00	0·223
390	8·25	3·25	0·236
600	7·75	2·75	0·230
1020	6·60	1·60	0·230
		Mean	0·280

TABLE IV.

$CH_2Br.\ COONa = 0{\cdot}001$ M; $Na_2S_2O_3 = 0{\cdot}0025$ M ;

Ionic concentration $= 0{\cdot}0085\ \mu$; 100 c. c. titrated.

0	24·40	9·40	—
120	23·00	8·00	0·2407
180	22·45	7·45	0·240
240	21·90	6·90	0·243
480	20·15	5·15	0·246
600	19·50	4·50	0·246
		Mean	0·243

TABLE V.

$CH_2Br\ COONa = 0{\cdot}004$ M; $Na_2S_2O_3 = 0{\cdot}002$ M;

Ionic concentration $= 0{\cdot}01\ \mu$; 50 c. c. titrated.

0	9·6	19·60	—
60	8·35	18·35	0·2665
120	7·35	17·35	0·2610
180	6·45	16·45	0·2680
240	5·75	15·75	0·2665
480	3·70	13·70	0·2690
		Mean	0·2662

TABLE VI.

$CH_2Br\ COONa = 0{\cdot}002$ M; $Na_2S_2O_3 = 0{\cdot}004$ M;

Ionic concentration $= 0{\cdot}014\ \mu$; 25 c. c. titrated.

Time in min.	C.c. $Na_2S_2O_3$	bromacetate.	K
0	9·60	4·60	—
60	9·00	4·00	0·2715
120	8·50	3·50	0·2750
180	8·10	3·10	0·2710
300	7·40	2·40	0·2825
450	6·85	1·85	0·2765
			Mean 0·2753

TABLE VII.

$CH_2Br\ COONa = 0{\cdot}008$ M; $Na_2S_2O_3 = 0{\cdot}004$ M;

Ionic concentration $= 0{\cdot}020\ \mu$; 25 c. c. titrated.

0	19·60	9·60	—
60	17·71	7·71	0·2980
90	16·25	6·25	0·2915
120	15·55	5·55	0·2862
150	14·90	4·90	0·2882
180	14·35	4·35	0·2892
		Mean	0·2906

TABLE VIII.

μ	K_{30}	K_{40}	K_{50}
0·0025	0·196	0·440	0·986
0·0050	0·214	0·498	1·150
0·0070	0·230	0·523	1·213
0·0085	0·244	0·540	1·260
0·0100	0·266	0·577	1·320
0·0140	0·275	0·661	1·480
0·0200	0·291	0·678	1·600
0·0280	0·310	—	—
0·0350	0·335	0·760	1·800
0·0500	0·391	0·866	1·946
0·0700	0·429	0·940	2·086
0·0850	0·460	0·989	2·250
0·1000	0·494	—	—

Discussion of results.

Fig. I gives the curve obtained by plotting $\log(K_{30} \times 10)$ as ordinates against $\sqrt{\mu}$ as abscisae. Examination of the curve shows that from $\sqrt{\mu}=0{\cdot}05$ to $\sqrt{\mu}=0{\cdot}125$ it is a good straight line and from the latter point its course deviates and then again it goes as a straight line with a lesser slope.

Rewriting equation (3)

$$\log K = \log K_1 + Z_A Z_B \sqrt{\mu}$$

we see that this equation demands that log K plotted against $\sqrt{\mu}$ should be a straight line with a slope equal to $Z_A Z_B$. This should be the case if in Debye's equation $-\log f = \alpha Z^2 \sqrt{\mu}$, the factor α has a value equal to 0·50 which will be so only in the neighbourhood of 20°. Approximately α has values 0·518 at 30°, 0·529 at 40° and 0·549 at 50°. If we use these values for α and make the necessary calculations, we would find that the slopes of the curves in the ideal region should be 2·072, 2·116 and 2·196 at 30°, 40°, and 50° respectively. The slope of the curve in Fig. I up to ionic strength $0{\cdot}014\mu$ (approximately) at 30° is actually 2·16, while curves drawn with results at 40° and 50° have slopes in this region 2·3 and 2·34 respectively. It is rather difficult to expect much closer agreement with theory from velocity measurements. These results indicate clearly therefore that so far as the ions involved in this reaction are concerned, Debye's equation holds good quantitatively up to a region of ionic strength $0{\cdot}015\ \mu$.

It is also of interest that beyond the point $0{\cdot}015\mu$, upto about $0{\cdot}10\ \mu$, the curve obtained by plotting log K against $\sqrt{\mu}$ is again a straight line with a slope equal to 1·31. The region upto $0{\cdot}01\mu$ is generally regarded as the ideal region for dilute solutions. In their theory of electrolytes Debye and Huckel do not however confine themselves to this ideal region ; they have also tried to account for the behaviour of electrolytes above this region by making certain simplifying assumptions. With the introduction of these simplifying factors, the expression for the activity coefficient of an ion undergoes modification and takes the form,

$$-\log f = \alpha\sqrt{\mu} + b\mu.$$

where b is again another constant. Wynne Jones (*J. Chem. Soc.*, 1928, **133**, 1282) has pointed out that the introduction of these linear terms

lowers the kinetic activity factor to approximately 2/3 its value in the ideal region, upto about 0·10 N. The slope of the curve in this region, in accordance with this modification, should be about 1·33 which is strikingly coincident with the value obtained experimentally (Fig. I gives in this region $\frac{d \log K}{d\sqrt{\mu}} = 1{\cdot}31$).

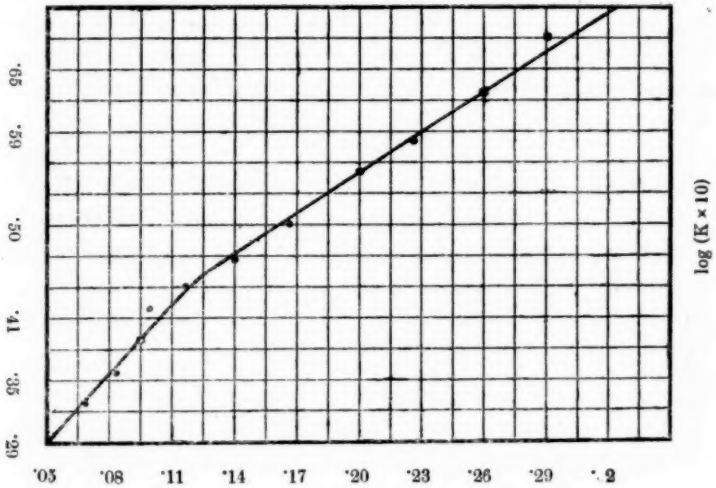


Fig. I

Temperature Coefficient of the Reaction.

It was observed in Part I (this *Journal*, 1928, **5**, 293) that the temperature coefficient of velocity constant was pretty constant at all concentrations and had the same value on either side of 60° for a rise of 10°C. It will be observed from Table VIII, that in the reaction between sodium monobromacetate and thiosulphate as well, the temperature coefficient of velocity constant on either side of 40° and at different ionic strengths has almost the same value, within narrow limits 2·2—2·3, for a rise in te nperature of 10°. This means that the variation of the kinetic activity factor with total ionic concentration, with reference to its value at any given concentration, is the same at all these temperatures. This may again be interpreted to mean that so far as any one of the ions involved in this reaction is concerned, the temperature coefficient of its activity coefficient is the same at all concentrations. This inference finds theoretical support from the equations of Debye and Ghosh.

$$-\log f \propto \frac{1}{(DT)^{\frac{3}{2}}} \quad \ldots \quad \ldots \quad \text{(Debye)}$$

$$-\log f \propto \frac{1}{DT} \quad \ldots \quad \ldots \quad \text{(Ghosh)}$$

where D is the dielectric constant of the ionising medium and T, the absolute temperature. Taking the values determined by Kockel (*Ann. Phys.*, 1925, **77**, 430) for the dielectric constant of water at different temperature, it is found on calculation that the product DT gradually, but only to a very small extent, falls as the temperature rises from 20° to 90° as can be seen from Table IX.

TABLE IX.

Temp. ...	20°	30°	70°	90°
$D \times T$ ...	$2{\cdot}335 \times 10^4$	$2{\cdot}305 \times 10^4$	$2{\cdot}155 \times 10^4$	$2{\cdot}113 \times 10^4$

This shows that although there would be an unmistakeable variation in $-\log f$ with variation in temperature, that would only be very small. The steadiness of the value of the temperature coefficient of the reaction rate thus becomes understandable.

Summary.

Velocity measurements of ionic reactions serve to test the validity of Debye-Huckel limitation law for electrolytes on the basis of Brönsted's and Soper's theories.

Kinetics of the reaction between sodium monobromacetate and sodium thiosulphate have been studied at 30°, 40° and 50° over the range of total ionic concentration between 0·0025 μ and 0·10 μ.

It has been found that so far as the ions involved in this reaction are concerned, Debye's equation for the activity coefficient of an ion accurately predicts the course of the reaction with variation in ionic strength upto 0·015 μ.

Temperature coefficient of the reaction rate has been found to be the same at all ionic concentrations. This is in accordance with the demands of Debye's and Ghosh's equations.

It gives me great pleasure to express my gratitude to Professor J. C. Ghosh for the interest he has taken in this work.

UNIVERSITY OF DACCA. *Received October* 15, 1928.

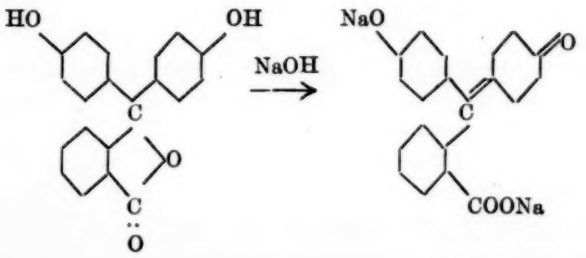
Aldehydo-phenolphthalein and Dyes derived from it.

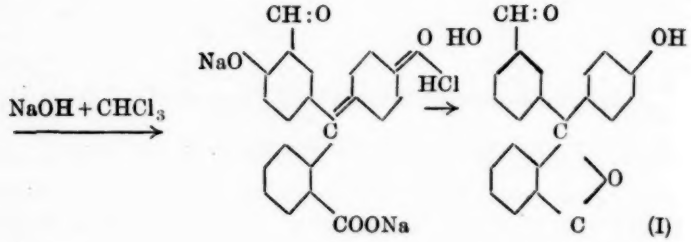
By Rajendra Nath Sen and Kali Charan Kar.

Although various derivatives of phenolphthalein were previously studied by different authors, it appears that no attempt has hitherto been made to obtain an aldehyde by the application of Reimer-Tiemann's reaction to it. The present work is mainly a study of the aldehyde, obtained by subjecting phenolphthalein to the above reaction with certain modifications, and also of a few interesting dyes derived from it.

It is interesting to note that the introduction of the aldehyde group into the phenolphthalein molecule produces marked changes in its properties. While the solubility of the aldehyde in alcohol, ether and chloroform is much greater than that of phenolphthalein, its melting point (97°-99°) is much lower than that of phenolphthalein (250°). The phenolphthalein molecule contains only one chromophore group and is colourless in the lactone form, but the aldehyde, containing an additional chromophore, C:O, shows a slight yellow colour. The alkaline solution of the aldehyde is more deeply coloured (red) than that of phenolphthalein (pink). The aldehyde reduces an ammoniacal solution of silver nitrate, but it does not reduce Fehling's solution.

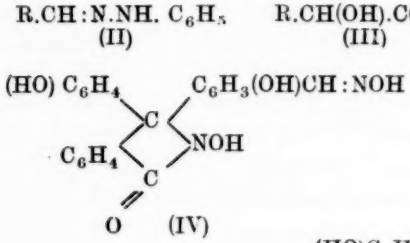
The structure, given to aldehydo-phenolphthalein or phenol-salicyl-aldehydo-phthalein (I) is evident from the fact that phenolphthalein in alkaline solution in which Reimer-Tiemann's reaction takes place, apparently contains only one hydroxyl group of which the *para*-position is occupied, and the two *ortho*-positions are identical, thus:

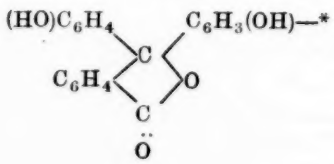




The formula of the compound is fully supported by the analysis of the aldehyde itself, and also of its various derivatives, described in this paper.

The aldehyde gives a phenyl-hydrazone (II) and a benzoin condensation product (III) in the usual manner; and a dioxime (IV) in an alkaline medium in which phenolphthalein itself forms an oxime. (*Ber.*, 1893, **26**, 172; *ibid*, 1895, **28**, 3258; Ornderff and Murray, *J. Amer. Chem. Soc.*, 1917, **39**, 679).



where R is 

Aldedehydophenolphthalein, like 6-aldehydo-coumarin (Sen and Chakravarti, *J. Amer. Chem. Soc.*, 1928, **50**, 2428) gives rise to various interesting dyes by its comdensation with different aromatic amino and hydroxy compounds. Thus several azomethine dyes have been obtained by condensing the aldehyde with (*i*) monoamines such as *p*-toluidine, *β*-napthylamine and amino-azo-benzene, (*ii*) diamines such as benzidine, *o*- and *p*-phenylenediamine, and (*iii*) such dyes as rosaniline, chrysoidine and safranine, containing free

* This radicle will be called "phenolphthaleinyl."

amino groups. In each of these cases the amine takes up as many molecules of the aldehyde as there are free amino groups present in it. The azomethine dyes, thus formed, are usually hydrolysed by warming with dil. mineral acids, and they dye wool and silk with shades, ranging from light yellow to bluish-red. It is also interesting to note that the condensation of the aldehyde with such dyes as rosaniline, chrysoidine and safranine produces a diminution in the intensity of colour, owing, perhaps, to the elimination of the auxochromic effect of the free amino groups in them.

Pyronine dyes have been obtained by condensing the aldehyde with diethyl-*m*-aminophenol and such hydroxy compounds as resorcin, pyrogallol, hydroquinone and *β*-naphthol in presence of conc. H_2SO_4 (sp. gr. 1·84) at 100° in the manner described by Sen and Sinha (*J. Amer. Chem. Soc.*, 1923, **45**, 2984). In these condensations one mol. of the aldehyde takes up two mols. of the hydroxy compounds, the second carbonyl group in the phenolphthalein residue of the aldehyde remaining inactive in each case. All these compounds form potassium salts, and the condensation product of the aldehyde with diethyl-*m*-aminophenol is soluble both in acids and alkalis, and that with resorcinol gives a bromo-derivative which dyes a brilliant red on silk and wool.

Triphenylmethane dyes have been obtained by condensing the aldehyde with dimethyl-aniline and *o*-cresotinic acid. In the first case conc. hydrochloric acid is used as the condensing agent at the temperature of boiling water-bath and tetramethyl-diamino-diphenyl-phenolphthalein-methane, $RCH=[C_6H_4N(CH_3)_2]_2$ is obtained. This leuco-base has no dyeing property, but when it is oxidised with lead-peroxide in the usual manner, it gives a fine bluish-green dye (phenolphthalein-green) which is of much interest on account of the presence of the lactone ring, associated with the basic group $N(CH_3)_2$, the compound being soluble both in acids and alkalis. The condensation with *o*-cresotinic acid is effected in presence of conc. H_2SO_4 (sp. gr. 1·84) in the cold, and the leuco base, di-methyl-dihydroxy-dicarboxylic-diphenyl-phenolphthalein-methane, $RCH=[C_6H_2(OH)(COOH)(CH_3)]_2$ is obtained as a yellowish product, having no dyeing property, but producing a fine red dye deepening to black on after-chroming, when the leuco base is oxidised with nitrosyl sulphate.

Thus it is found that phenolphthalein which is colourless and possesses no dyeing property, gives rise to various beautiful and

interesting dyes if it is converted into an aldehyde and then condensed with the different aromatic amino and hydroxy compounds.

Experimental.

Preparation of Aldehydo-phenolphthalein.

Phenolphthalein (12·5 g.) is dissolved in sodium hydroxide solution (16 g. in 32 c.c. of water) and the solution heated under reflux on the boiling water-bath with frequent addition of chloroform (14 c.c. in all) in course of 12 hours. The excess of chloroform is driven off on the water-bath, cooled, diluted with water and acidified with dilute hydrochloric acid. The precipitate is filtered off, washed with water, dried, and extracted with ether which dissolves the whole of the aldehyde and a part of the unaltered phenolphthalein. The residue, after evaporating off the ether, is extracted with chloroform in which phenolphthalein is practically insoluble, and the aldehyde readily goes into solution. The chloroform-solution is evaporated, and the residue is crystallised from dilute alcohol in the form of a slightly yellowish microcrystalline powder (m.p. 97°-99°), readily soluble in ethyl alcohol, ether, chloroform, acetone, glacial acetic acid, NaOH, and Na_2CO_3 solutions; insoluble in benzene, carbon tetrachloride, carbon bisulphide, petroleum ether and dilute acids (yield about 20% of theoretical). (Found: C, 72·61; H, 4·16. $C_{21}H_{14}O_5$ requires C, 72·85; H, 4·04 per cent.).

Derivatives of Aldehydo-phenolphthalein.

The *phenylhydrazone* was prepared in glacial acetic acid medium by heating for half an hour on the water-bath. The precipitate, obtained by pouring the solution into cold water, is filtered, washed with water, dried and extracted with benzene; the benzene solution evaporated, and the residue crystallised from dilute alcohol in the form of yellow micro-crystalline powder, melting at 148°. It is soluble in ethyl alcohol, chloroform, acetone, benzene and ether; insoluble in carbon tetrachloride, carbon bisulphide, and petroleum ether. Aqueous caustic soda and sodium carbonate dissolve it giving violet solutions. Yield theoretical. (Found: N, 6·32. $C_{27}H_{20}N_2O_4$ requires N, 6·42 per cent.)

The dioxime.—The aldehyde, dissolved in aqueous caustic soda, is added to an aqueous solution of hydroxylamine hydrochloride. The mixture is heated on the water-bath at 80° for an hour,

the solution cooled, and acidified with dilute acetic acid. The precipitate is washed with dilute acetic acid and finally with warm water, and crystallised from dilute alcohol in the form of a yellow microcrystalline powder, decomposing at 235°. It is soluble in alcohol, acetone and ether. Yield about 90 per cent. (Found: N, 7·26. $C_{21}H_{16}O_5N_2$ requires N, 7·44 per cent.).

Phenolphthaleinoin was prepared in the usual manner like benzoin, and crystallised from dilute alcohol as a yellow microcrystalline powder, melting at 152°, and soluble in ethyl alcohol, methyl alcohol, acetone, glacial acetic acid, ether and chloroform. It reduces Fehling's solution. (Found: C, 72·66; H, 4·17. $C_{42}H_{28}O_{10}$ requires C, 72·83; H, 4·04 per cent.).

Dyes Derived from Phenolphthalein.

Azo-methine dyes.

Phenolphthaleinal-toluidine (para).—The aldehyde (3 g.) and *p*-toluidine (2 g.) separately dissolved in hot alcohol, are mixed together, heated on the water-bath under reflux for an hour, cooled, poured into water, and the precipitate filtered off. It is dissolved in ammonia, filtered, the filtrate acidified with acetic acid, and the precipitate collected and washed with dilute alchohol (1:4). The residue is crystallised from alcohol as a light orange powder, m.p. 140°. It is soluble in ethyl alcohol, methyl alcohol, acetone, ether, chloroform and glacial acetic acid, and insoluble in benzene, carbon bisulphide, carbon tetrachloride and petroleum ether. Yield 90 per cent. (Found: N, 3·24. $C_{28}H_{21}O_4N$ requires N, 3·21 per cent).

Other azo-methine dyes prepared are listed in Table A.

Pyronine Dyes.

(1) *Diresorcinol-phenolphthaleinein.*

The aldehyde (3 g.) and resorcin (2·5 g.) are made into a paste with 1 c.c. of concentrated sulphuric acid (sp. gr. 1·84) and heated with an air-condenser on the boiling water-bath for 5 hours. It is cooled, dissolved in sodium carbonate solution, filtered; the filtrate is acidified with conc. HCl, allowed to stand overnight, and again filtered. The residue is washed with water, dried, digested with ether, and filtered; the residue, thus obtained, is crystallised from dilute alcohol as an orange powder, soluble in alcohol and acetone, and insoluble in

ether, chloroform, benzene and petroleum ether. The alkaline and alcoholic solutions of the substance show green fluorescence. Yield 60 per cent. (Found: C, 74·76; H, 4·26. $C_{33}H_{20}O_7$ requires C, 75; H, 3·8 per cent.).

The *tripotassium salt* is obtained as a red crystalline powder by dissolving the substance in requisite quantity of aqueous caustic potash, and subsequently washing the dry salt with absolute alcohol. It dyes wool and silk deep yellow shade. (Found: K, 18·14. $C_{33}H_{17}O_7K_3$ requires K, 18·22 per cent.).

Other pyronine dyes prepared, together with their derivatives, are listed in Table B.

Triphenylmethane Dyes.

(1) *Tetra-methyl-diamino-diphenyl-phenolphthalein-methane.*—The aldehyde (3 g.) is dissolved in 10 c.c. of dimethyl-aniline, 5 c.c. of conc. HCl are added, and the whole heated on the boiling water-bath with an air-condenser for 24 hours, with frequent addition of conc. HCl (10 c.c. in all). The solution is cooled, made alkaline with caustic soda, and distilled in steam till the distillate is free from dimethyl-aniline. The solution in the distilling flask is carefully neutralised with dilute acetic acid, the white precipitate filtered off, dissolved in dilute HCl, and reprecipitated with dilute ammonia. It is filtered, washed with water, and crystallised from dilute alcohol as greenish-white plates softening at 187°. It is soluble in alcohol, ether, chloroform, acetone, glacial acetic acid, sodium carbonate and caustic soda solution; insoluble in benzene, carbon bisulphide, carbon tetrachloride, and petroleum ether. Yield 90 per cent. (Found: N, 4·90. $C_{37}H_{34}O_4N_2$ requires N, 4·91 per cent.).

The leuco-base as described above is oxidised with lead peroxide in the usual manner. The hydrochloride is a deep bluish-green substance, producing a bluish green shade on wool, and silk and tannin-mardanted cotton.

(2). *Dimethyl-dihydroxy-dicarboxylic-diphenyl-phenolphthalein-methane.*—The dry aldehyde (3 g.) and dry *o*-cresotinic acid (1·5 g.) are powdered together, made into a paste with 2 c.c. of concentrated sulphuric acid (sp. gr. 1·84), and allowed to stand over-night. The product is poured into cold water, filtered, the residue washed with water and disssolved in ammonia and filtered again; the filtrate is acidified with dilute acetic acid, the precipitate filtered off, washed

with water, and crystallised from dilute alcohol as yellowish plates, softening at 215° soluble in alcohol, ether, acetone, caustic soda, and sodium carbonate solution, insoluble in benzene carbon bisulphide, and petroleum ether. Yield 80 per cent. (Found: C, 69·89; H, 4·51. $C_{37}H_{28}O_{10}$ requires C, 70·25; H, 4·43 per cent.).

The leuco-base is oxidised with nitrosylsulphate at 50°-60°, when a red product is obtained. It dyes wool a red shade which deepens to black when it is after-chromed.

Summary.

(1) Aldehydo-phenolphthalein or phenol-salicyl-aldehydophthalein (m.p. 97°-99°) has been prepared by the application of Reimer-Tiemann's reaction to phenolphthalein; it gives a phenylhydrazone and a dioxime and undergoes benzoin condensation in the usual manner.

(2) Interesting azo-methine dyes have been obtained by the condensation of aldehydo-phenolphthalein with *p*-toluidine, *β*-naphthylamine, amino-azo-benzene, benzidine, *o*- and *p*-phenylene-diamine and with dyes such as rosaniline, chrysoidine and safranine which contain free amino groups.

(3) Brilliant pyronine dyes have been obtained by condensing the aldehyde with diethyl-*m*-amino-phenol, *β*-naphthol, resorcinol, hydroquinone and pyrogallol in presence of concentrated sulphuric acid. The aldehyde group reacts in these condensations, the C:O group in the lactone ring remaining inactive.

(4) Beautiful triphenylmethane dyes have been obtained by condensing the aldehyde with dimethylaniline and *o*-cresotinic acid.

TABLE A.

Name.	Formula.	Method of preparation.	M.p. and appearance.	Analysis : P.c. of N. Calc.	Found.	Properties.
Phenolphthaleinal—		Aldehydo-phenolphthalein				
naphthyl-amine (β).	$R^*CH=NC_{10}H_7$	+ β-naphthyl-amine (in alcohol) on water-bath for an hour. Yield 90 %.	154°; yellow microcrystalline powder.	2·97	2·87	Soluble in alcohol, acetone, ether, chloroform, and glacial acetic acid; hydrolysed by hot-mineral acids; light yellow shade on wool and silk.
-amino-azo-benzene ...	$RCH=NC_6H_4N:N.C_6H_5$	+ amino-azo-benzene (in alcohol) on water-bath for an hour. Yield 90 %.	235° d; red microcrystalline powder.	8	7·93	Soluble in alcohol, acetone, glacial acetic acid; sparingly soluble in ether and chloroform; hydrolysed by warm moderately strong mineral acids; yellow shade on wool and silk.
-benzidine ...	$RCH=N.C_6H_4.C_6H_4.N=CHR.$	+ benzidine (in alcohol) on water-bath for an hour. Yield 80 %.	191°; orange powder from alcohol; microcrystalline.	3·33	3·26	Soluble in acetone, moderately in alcohol, ether, chloroform and glacial acetic acid; insoluble in benzene; hydrolysed by hot mineral acids with difficulty; orange shade on wool and silk.
-p-phenylene-diamine ...	$RCH=NC_6H_4.N=CHR$	+ p-phenylene-diamine (in alcohol) on water-bath for an hour. Yield 70 %.	230° (softens); yellowish brown powder from alcohol.	3·66	3·51	Soluble in acetone, moderately in alcohol, glacial acetic acid, chloroform and ether; insoluble in benzene; hydrolysed by mineral acids; light-orange shade on wool and silk.

TABLE A—*contd.*

Name.	Formula.	Method of preparation.	M.p. and appearance.	Analysis: P.c. of N. Calc.	Found.	Properties.
Phenolphthaleinal—		**Aldehydo-phenolphthalein—**				
-*o*-phenylene-diamine ...	$RCH=N.C_6H_4.N=CHR$	+ *o*-phenylene-diamine (in alcohol, on water-bath for an hour. Yield 80 %.	218°; yellow microcrystalline powder from alcohol.	3·66	3·64	Readily soluble in alcohol, acetone and glacial acetic acid; moderately soluble in chloroform and ether; insoluble in benzene; hydrolysed by warm strong mineral acids; straw-yellow shade on wool and silk.
-chrysoidine ...	$RCH=N.C_6H_3(N:NC_6H_5)$ $\vert$ $N=CHR$	+ chrysoidine + (alcohol) on water-bath for an hour. Yield 90 %.	Red microcrystalline powder from alcohol.	6·45	6·32	Soluble in alcohol, acetone, ether, chloroform, and glacial acetic acid; insoluble in benzene; hydrolysed by hot mineral acids; yellowish-brown shade on wool and silk.
safranine	$[RCH=N.C_6H_3(CH_3)N]_2$	+ safranine + (alcohol) on water-bath for an hour. Yield 90 %.	,,	5·65	5·60	Readily soluble in alcohol, acetone and glacial acetic acid; moderately soluble in benzene, ether and chloroform; hydrolysed by hot mineral acids; scarlet-red shade on wool and silk.
-rosaniline ...	$RCH=N.C_6H_4C_6H_3(CH_3)N=CHR.$ $\vert$ $N=CH.R$ (OH)	+ rosaniline + (alcohol) on water-bath for an hour. Yield 85 %.	Violet-red powder from alcohol.	3·22	3·14	Soluble in alcohol, acetone, glacial acetic acid, sparingly soluble in chloroform, and ether; brilliant red shade on wool and silk.

* $R=C_{10}H_{11}O_4$.

TABLE B.

Name.	Formula.	Method of preparation.	M.p. and appearance.	Analysis (%). Calc.	Found.	Properties.
Phenolphthaleinein—di-naphthol (β) ...	$C_{41}H_{24}O_5$	The aldehyde—+β-naphthol + (conc. H_2SO_4) on water-bath for 5 hours. Yield 80 %.	260° d; greyish powder.	C, 82·55 H, 4·02	82·49 4·41	Soluble in alcohol, and acetone, insoluble in ether, chloroform and benzene; alkaline solution shows no fluorescence, has very little dyeing property.
Mono-potassium salt ...	$C_{41}H_{23}O_5K$	β-naphthol-phenolphthaleinein + aqueous KOH, dry salt washed with absolute alcohol.	Red crystalline powder.	K, 6·15	6·30	.....
-dihydroquinone ...	$C_{32}H_{20}O_7$	The aldehyde + hydroquinone (conc. H_2SO_4) on water-bath for 5 hours. Yield 80 %.	250° d; greyish black powder.	C, 75 H, 3·8	74·59 4·24	Soluble in alcohol, and acetone, insoluble in ether chloroform, and benzene; alkaline solution shows a slight yellowish-green fluorescence; dyes wool and silk a light brown shade.
Tripotassium salt ...	$C_{32}H_{17}O_7K_3$	In the usual manner	.....	K, 18·22	18·03	.....

TABLE B—*contd.*

Name.	Formula.	Method of preparation.	M.p. and appearance.	Analysis (%). Calc.	Found.	Properties.
Phenolphthaleinein—di-pyrogallol	$C_{33}H_{20}O_9$	The aldehyde + pyrogallol, + (conc. H_2SO_4) on water-bath for 5 hours. Yield 65 %.	260° d; greyish black powder.	C, 70·71 H, 3·5	70·36 3·66	Soluble in alcohol and glacial acetic acid; insoluble in ether, chloroform, and benzene; alkaline solution not fluorescent; dyes aluminium-mordanted wool dark-brown, and iron-mordanted wool greyish-black.
Phenolphthaleinal-rhodamine.	$C_{41}H_{33}N_3O_5$	The aldehyde + diethyl-*m*-aminophenol (conc. H_2SO_4); on water-bath for 5 hours. Yield 90 %.	Violet powder.	N, 4·39	4·61	Soluble both in acids and alkalis, also in alcohol, acetone, glacial acetic acid; moderately soluble in ether, chloroform; insoluble in benzene, petroleum ether. Red shade on wool and silk.

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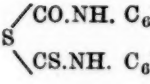
Formation of Heterocyclic Compounds from Diethyl-Xanthic-Formic Ester.

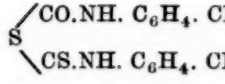
By Praphulla Chandra Guha and Devendra Nath Dutta.

Diethylxanthic-formic ester, $EtO_2C.S.CSOEt$ was prepared by Holmberg (*J. pr. Chem.*, 1905, **71**, 264) by the action of chlorocarbonic ester upon potassium ethyl xanthate. Some similar other compounds, *viz.*, diethylxanthic acetic ester and ethylxanthic-propionic acid and their calcium, barium and sodium salts had also been prepared by the same author. This appears to be all about the di-esters of this nature and their reactions as studied up to this time. Ethylxanthic-formic ester contains two active ester groups, so it was thought advisable to utilise this compound as a reagent for the building up of heterocyclic compounds. With this object in view its action upon bases like amines, hydrazines, diamines, semi- and thiosemi-carbazides has been studied and as will be seen the object has been amply realised.

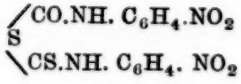
The primary amines, *e. g.*, aniline, *o*- and *p*-toluidines, *m*- and *p*-nitranilines and *β*-naphthylamine react readily with the diester to yield the corresponding thiodicarbon-monothio-diarylamides and thus the following compounds (I-VI) have been obtained:



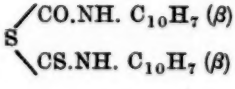
(I)



(II & III)
(*ortho* and *para*)



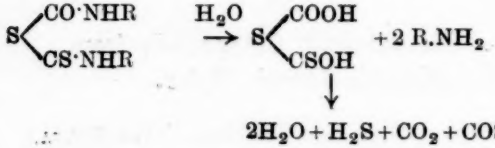
(IV & V)
(*meta* and *para*)



(VI)

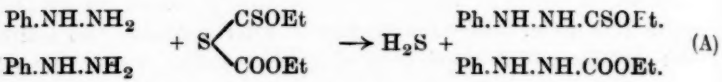
The diarylamides form diacetyl derivatives and instead of forming disulphides by the oxidising action of ferric chloride, form simple iron salts and are indifferent to the action of iodine and potassium ferricyanide. They are decomposed on being boiled with

strong hydrochloric acid into carbon dioxide, carbon oxysulphide, sulphuretted hydrogen and arylamines, thus:



$$2H_2O + H_2S + CO_2 + COS.$$

It was expected by analogy with the action of the arylamines that two molecules of phenylhydrazine should react with one molecule of the ester to yield a diphenylhydrazide. But the compound actually isolated is monothio-phenylcarbazinic ester ($C_6H_5.NH.NH.CSOC_2H_5$). So, it was assumed that the reaction had proceeded thus:—

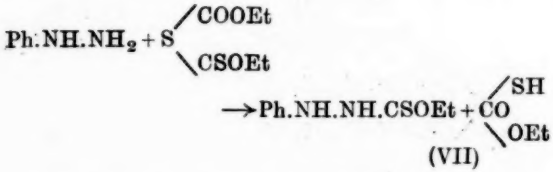


(A)

and it is well known that acidyl sulphides like $S(COCH_3)_2$ and $S(COC_6H_5)_2$ react with ammonia, amines, hydrazines, etc., to yield amides and hydrazides thus:

$$2NH_3 + S(OCR)_2 = H_2S + 2\ R.CONH_2$$

The explanation as to the course of the reaction expressed in equation (A) appears to require some modification as the other product of the reaction, *viz.*, $C_6H_5.NH.NH.COOC_2H_5$ could not be traced and also because of the fact that carbon dioxide was proved to be one of the products of the reaction. The equation which can explain all these facts appears to be as given below:

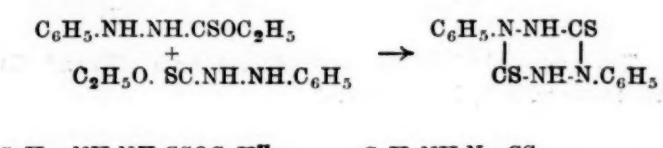


(VII)

The thiocarbonic ester being unstable is hydrolysed into alcohol, carbon dioxide and sulphuretted hydrogen.

By analogy with the formation of diphenylurazine by the action of heat upon phenylcarbazinic ester (*Ber.*, 1888, **21**, 2329;

Annalen, 1891, **263**, 282 ; *Ber.*, 1896, **29**, 829) it was expected that phenylcarbazinic-monothio ester, $C_6H_5.NH.NH.CSOC_2H_5$, should also yield diphenyldithio-*p*-urazine or *N*-phenyl-*N*-anilinodithiourazole, thus :

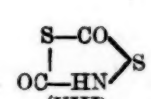


N-phenyl-*N*-anilinodithiourazole.

But the reaction was very complicated and yielded a tarry mass from which nothing could be separated in a state of purity. At 140°—150° the ester was partially decomposed and from the reaction mixture most of the unreacted substance was recovered and at still lower temperature (110°-115°) the ester was found to remain unchanged.

The action of aqueous potassium hydroxide (20%) was next studied and it was found that the ester gets decomposed into phenylhydrazine, alcohol and potassium salt of thiocarbonic acid from the last of which sulphuretted hydrogen was evolved during acidification.

The action of strong hydrochloric acid upon the ester, $C_6H_5.NH.NH.CSOC_2H_5$, was however, attended with success and a heterocyclic five-membered compound (VIII) containing two sulphur atoms in the ring was obtained.

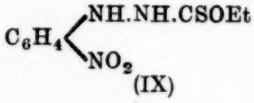


(VIII)

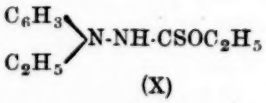
That the two sulphur atoms in compound (VIII) form members of the ring is proved by the fact that they can neither be desulphurised with mercuric oxide nor can they yield disulphide with iodine.

The action of *p*-nitrophenylhydrazine and unsym-phenylethylhydrazine was also tried ; they yielded the corresponding

monothio-carbazinic esters (IX) and (X) as in the case of phenylhydrazine.



(IX)



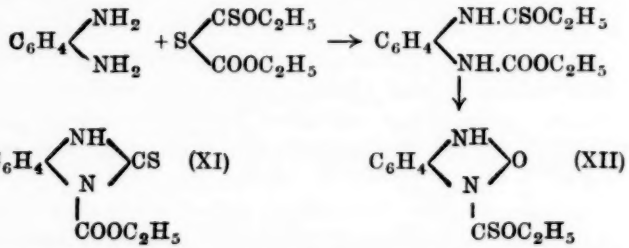
(X)

The compound (VIII) was also obtained from (IX) and (X) on treatment with hydrochloric acid.

Action of Diamines.

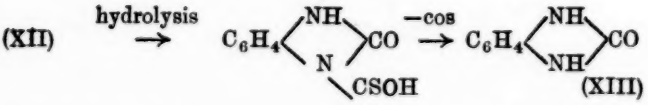
The reaction of *o*-phenylene diamine with the ester is interesting and is attended with the formation of three compounds, *viz.* (XI), (XII) and (XIII).

Firstly *o*-phenylene monothiodiurethane* is formed which under the conditions of the experiment suffers internal condensation in two different ways yielding *N*-carbethoxy-phenylene thiourea (XI) and *N*-thiocarbethoxy-phenylene urea (XII) thus:



(XI) (XII)

The formation of phenylene urea (XIII) can be explained in the assumption that compound (XII) is first hydrolysed and then loses a molecule of carbon oxysulphide.

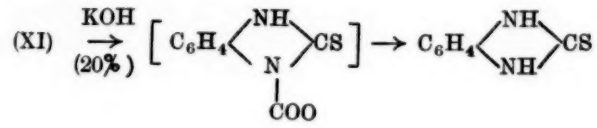


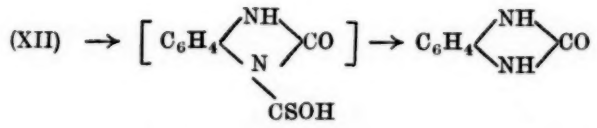
(XIII)

The correctness of the formulae (XI) and (XII) has been established by the facts gathered from a study of the action of potassium

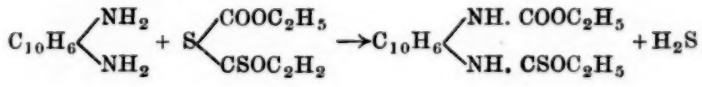
* A compound of the type of (XVI) has actually been isolated with ethylene diamine.

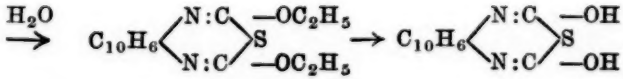
hydroxide solution (20%) upon them when phenylene thiourea and phenylene urea are obtained respectively from (XI) and (XII), thus:

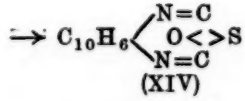




The action of 1:2-naphthylene diamine has also been studied but its behaviour with the diester appears to be a little peculiar † in so far as the two products finally isolated are of a quite different nature from compounds (XI, XII & XIII). Two compounds, 4:5-naphthylene-2:7-endoxy-1:3:6-thioheptadiazine (XIV) and 1-carbethoxyamido-naphthyl-4:5-naphthylene-2:7-endoxy-1:3:6-heptatriazine (XV) are formed in this case; the formation of (XIV) can be best explained thus:







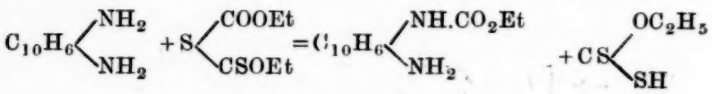
(XIV)

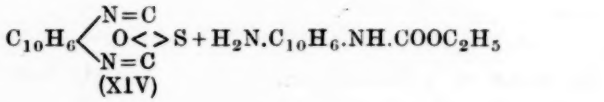
That the sulphur atom of compound (XIV) is a member of the ring is proved by the fact that it cannot be desulphurised on treatment with mercuric oxide; moreover the absence of any group like (NH—CO—) or (NH—CS) is proved by the fact that the compound

† It will be seen that the experiments with phenylene and naphthylene diamines have not been conducted under identical conditions (*vide Experimental*).

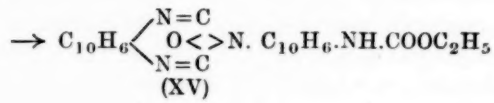
is insoluble in alkali (compare compounds XI-XIII which are all soluble in alkali).

As regards the formation of the heptatriazine compound, it appears to be essential to assume, first of all, the formation of 1-amido-2-carbethoxyamido-naphthalene, $NH_2.C_{10}H_6.NH.CO_2Et$ which in its turn acting upon (XIV) produces compound (XV).





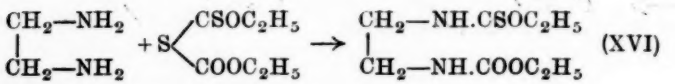
(XIV)



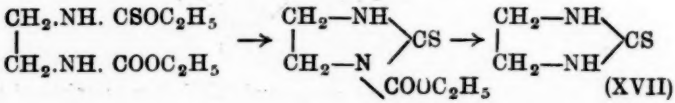
(XV)

Such replacement of sulphur by a nitrogen atom by the action of ammonia and amines is well known in heterocyclic chemistry.

The action of one diamine of the aliphatic series, *viz.*, ethylene diamine has also been studied when ethylene monothiodiurethane (XVI) and ethylene thiourea (XVII) are simultaneously formed thus:



(XVI)



(XVII)

The above equation regarding the formation of (XVII) from (XVI) has been further confirmed from a study of the action of hydrochloric acid upon (XVI) when ethylene thiourea is obtained. (Compare the formation of phenylene thiourea from *N*-carbethoxy phenylene thiourea.)

Phenylene and ethylene thiourea could up to this time be obtained only by heating *o*-phenylene disulphocyanide (Lellmann, *Annalen*, 1883, **221**, 8) and the thiocarbamic acid derivative obtained from ethylene diamine and carbon disulphide (Hoffmann, *Ber.*, 1872, **5**, 242) at the temperature of boiling water.

Action of semi- and thiosemi-carbazides.

Semicarbazide reacts with the diester to yield semicarbazide monothio-carboxylic ethyl ester, $NH_2—CO—NH—NH—CSOC_2H_5$ (XVIII). It is interesting to note that the behaviour of thiosemicarbazide and 4-arylthiosemicarbazides towards the diester is different from that of semicarbazide. Semicarbazide yields the corresponding monothiocarbonic ester, whereas thiosemicarbazide and 4-arylthiosemicarbazides yield their carbonic esters.

$$NH_2.CO.NH.NH_2 \longrightarrow NH_2.CO.NH.NH.CO_2C_2H_5 \quad (XVIII).$$

$$NH_2.CS.NH.NH_2 \longrightarrow NH_2.CS.NH.NH.COOC_2H_5 \quad (XIX).$$

$$C_6H_5.NH.CS.NH_2 \longrightarrow O_6H_5NH.CS.NH.NH.COOC_2H_5 \quad (XX).$$

$$p\text{-}C_7H_7.NH.CS.NH.NH_2 \longrightarrow p\text{-}C_7H_7.NH.CS.NH.NH.CO_2Et \quad (XXI).$$

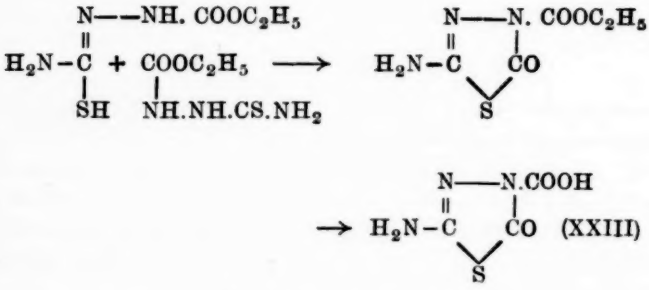
$$C_{10}H_7.NH.CS.NH.NH_2 \longrightarrow C_{10}H_7.NH.CS.NH.NH.COOC_2H_5 \quad (XXII).$$

It is probable that in each case both types of compounds (*viz.*, carbonic ester and thiocarbonic ester) are simultaneously formed of which the quantity of one preponderates over that of the other. From a perusal of the compounds (XVIII-XXII) a generalisation does not appear to be quite out of possibility. The remote (NH_2—CO) group of semicarbazide, being more negative in character as compared with the (NH_2.CS) group of thiosemicarbazide, facilitates the formation of $NH_2CO.NH.NH.CSOC_2H_5$; whereas NH_2.CS group of thiosemicarbazide being less negative, facilitates the formation of $NH_2.CS.NH.NH.COOC_2H_5$.

The behaviour of strong hydrochloric acid upon the semicarbazide and thiosemicarbazide compounds (XVIII and XIX) is also quite interesting; the former gets decomposed into alcohol, carbon

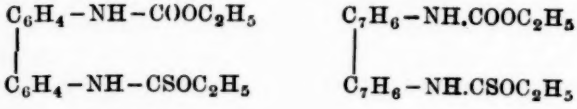
oxysulphide and semicarbazide ; whereas the latter yields 2-amino--carboxylic-5 keto-4 : 5-dihydro-1 : 3 : 4-thiodiazole (XXIII), thus :

$$NH_2.CO.NH.NH.CSOC_2H_5 \longrightarrow NH_2.CO.NH.NH_2 + H_2O + COS + C_2H_5OH$$



It liberates carbon dioxide from sodium bicarbonate and is readily soluble in sodium carbonate showing the presence of a carboxylic group, it does not form mercaptides with mercuric chloride and lead acetate, does not form disulphide with iodine, nor can it be desulphurised by treatment with mercuric oxide. All these reactions go to show that the sulphur atom is present not in the " SH " form, nor in the thioketonic form, " CS, " but it is present as a member of the ring. It forms a benzylidene derivative with benzaldehyde which shows that it contains an amino group.

Benzidine and tolidine form with the diester *p* : *p'*-diphenyl-monothiodiurethane (XXIV) and *p* : *p'*-ditolyl-monothiourethane (XXV).



(XXIV) (XXV)

Experimental.

Thiodicarbo-monothiodiphenylamide (I).

Diethylxanthic formic ester (4 g) dissolved in a small quantity of alcohol was cooled to 0° in an ice-bath and aniline (3·8 g.) was gradually added to it. Heat was evolved during the reaction with the

liberation of a small amount of sulphuretted hydrogen. For completion of the reaction the mixture was allowed to stand for two to three hours. It was then shaken with dilute hydrochloric acid to remove the excess of aniline. A solid separated at this stage which was filtered, washed with water and crystallised from dilute alcohol, m.p. 63°-64°. The substance is soluble in dilute alkali but insoluble in dilute acid. On being boiled with concentrated hydrochloric acid it decomposes into carbon dioxide, carbon oxysulphide and aniline hydrochloride. (Found: N, 9·82. $C_{14}H_{12}ON_2S_2$ requires N, 9·71 per cent.).

Behaviour towards Oxidising Agents.

The substance was heated with an excess of ferric chloride under reflux for about two hours after which the whole mass was allowed to cool. The separated crystalline green solid was repeatedly washed with ether to remove the adhering ferric chloride (neither water nor alcohol should be used for washing, for in the former case a tarry matter is formed whilst in the latter the substance passes into solution). The residue was crystallised from dilute alcohol. The substance is insoluble in alkali but the original substance is soluble in alkali. The test for iron in the compound was made by burning the substance. A brown residue always remained which responded to the usual tests for iron. So the substance is not oxidised by ferric chloride but its iron salt is only formed. The substance was found to be quite indifferent to the oxidising action of iodine and potassium ferricyanide.

Thiodicarbo-monothiodi-o-tolylamide (II).

An alcoholic solution of *o*-toluidine (2·2 g.) was gradually added to an alcoholic solution of the ester (2 g.). As the reaction proceeded with evolution of heat, it had to be moderated by cooling with cold water. A small quantity of sulphuetted hydrogen was evolved during the reaction. The mixure was allowed to stand at the room temperature for two to three hours for completion of reaction. It was then diluted with water and shaken with dilute hydrochloric acid to remove the excess of *o*-toluidine. A solid separated at this stage which after filtration and washing was crystallised from absolute alcohol, m. p. 205.° (Found : N, 8·91. $C_{16}H_{16}ON_2S_2$ requires N, 8·86 per cent.).

Thiodicarbo-monothiodi-p-*tolylamide* (III) was obtained in a similar manner. It crystallised from dilute alcohol, m. p. 85°. The compound is soluble in dilute alkali but insoluble in dilute acid. (Found: N, 8·52; S, 20·81; $C_{16}H_{16}ON_2S_2$ requires N, 8·86; S, 20·25 per cent.).

Thiodicarbon-monothiodi-m-*nitranilide* (IV).

m-Nitraniline (1·5 g.) was added to the ester (2 g.) dissolved in alcohol. As the reaction took place with evolution of heat, the mixture was cooled with ice water, traces of sulphuretted hydrogen were also detected. The mixture was allowed to stand at the ordinary temperature for two to three hours to bring the reaction to completion. It was then diluted with water and shaken repeatedly with warm dilute hydrochloric acid to remove the excess of *m*-nitraniline. The separated crystalline solid was filtered and crystallised from dilute alcohol, m. p. 105°. The substance is soluble in dilute alkali but insoluble in dilute acid. (Found: N, 14·52. $C_{14}H_{10}O_5N_4S_2$ requires N, 14·81 per cent.).

The *diacetyl derivative* was obtained by heating the substance for a short time with an excess of acetic anhydride. It crystallised from alcohol, m. p. 114°-115°. (Found: N, 12·42. $C_{18}H_{14}O_7N_4S_2$ requires N, 12·12 per cent.).

Thiodicarbon-monothiodi-p-*nitranilide* (V).

The method of preparation, and purification was the same as in the case of the previous compound. It melts at 95°-96°, and is soluble in dilute alkali but insoluble in acid. (Found: N, 14·65. $C_{14}H_{10}O_5N_4S_2$ requires N, 14·81 per cent.)

Thiodicarbon-monothiodi-β-naphthylamide (VI) obtained in a similar manner melts at 90°. It is insoluble in acid but soluble in alkali. (Found: N, 7·05. $C_{22}H_{16}ON_2S_2$ requires N, 7·21 per cent.)

Monothio-phenylcarbazinic ester (VII).

An alcoholic solution of phenylhydrazine (2·2 g.) was gradually added to the ester (2 g.) dissolved in alcohol under ice cooling when the reaction proceeded with evolution of sulphuretted hydrogen. For completion of the reaction the mixture was allowed to stand at the room temperature for two to three hours and then heated under reflux on a water-bath for half an hour more. The cold solution was

then shaken with dilute hydrochloric acid to remove the excess of phenylhydrazine. At this stage a solid separated which was crystallised from dilute alcohol, m. p. 73°-74°. It is soluble in alkali but insoluble in acid. (Found: N, 14·41. $C_9H_{12}ON_2S$ requires N, 14·28 per cent.).

The filtrate from the above carbazinic ester on evaporation gave a white crystalline substance which was very soluble in water and was proved to be phenylhydrazine hydrochloride.

Action of strong Hydrochloric Acid on (VII): *Formation of* (VIII).

The ester was heated under reflux with concentrated hydrochloric acid for half an hour when a clear solution was obtained. The solution on being cooled yielded a precipitate which was filtered, washed and crystallised from water, m.p. 135°. The substance is soluble in alkali and can be precipitated with acid. It does not give any disulphide with iodine and cannot be desulphurised with mercuric oxide. (Found: N, 10·2. $C_2HO_2NS_2$ requires N, 10·37 per cent.).

Action of Heat upon monothio-phenylcarbazinic ester.

About 5 gms. of the ester were heated in an oil-bath at 230°-240° for 3-4 hours when sulphuretted hydrogen was profusely evolved. A tarry mass was obtained on cooling. It was very much soluble in ether, acetone and benzene but slightly less soluble in alcohol. So the tarry mass was treated with alcohol when a very small amount of solid insufficient for purification separated. The reaction was repeated at 140°-150°, the period of heating remaining the same. In this case also a good quantity of tar was formed and a small quantity of the unchanged substance could only be recovered. At a still lower temperature (110°-115°) for fourteen hours the whole of it was found to remain unchanged.

Action of Potassium Hydroxide on (VII).

The ester was heated with aqueous caustic potash solution (20%) under reflux for about 45 minutes. The clear solution was then allowed to cool and then acidified with dilute hydrochloric acid. During acidification sulphuretted hydrogen was evolved profusely and a solid separated mixed with sulphur. The substance was freed from sulphur by extracting with benzene in which the substance is

very soluble. On evaporation of benzene, a solid was obtained which on examination was found to be nothing but the unchanged substance. The original filtrate gave test for phenylhydrazine. Evidently the monothiophenylcarbazinic ester gets decomposed into phenylhydrazine, alcohol, and potassium salt of thiocarbonic acid from the last of which sulphuretted hydrogen is evolved during acidification.

p-Nitrophenylcarbazinic-monothio-ethylester (IX).

p-Nitrophenylhydrazine under similar conditions of experiment as phenylhydrazine gives a similar type of compound. After crystallisation from alcohol it melts at 108°-109°. It is soluble in alkali but insoluble in acid. (Found: N, 17·61. $C_9H_{11}O_3N_3S$ requires N, 17·5 per cent.).

Action of strong Hydrochloric Acid on (IX): *Formation of* (VIII).

p-Nitrophenylcarbazinic-monothio ethyl ester was heated under reflux with concentrated hydrochloric acid for half an hour when the whole of it passed into solution. The solution was then allowed to cool when a solid separated. The mixture was then diluted with water when a part of the solid passed into solution. The residue was filtered, washed with cold water and crystallised from boiling water, m.p. 135°. The substance on analysis was found to be identical with compound (VIII). (Found: N, 10·50 per cent.).

Ethyl monothio-ethylphenylcarbazinic ester (X).

This was obtained similarly as the foregoing compound ; crystallised from alcohol it melted at 242°. (Found: N, 12·32. $C_{11}H_{16}ON_2S$ requires N, 12·50 per cent.).

Action of o-Phenylene diamine on Diethylxanthic formic ester: Formation of (XI), (XII) *and* (XIII).

An alcoholic solution of *o*-phenylene diamine (2 g.) was gradually added to the ester (4 g.) cooled to 0°. During the reaction, heat and H_2S were liberated. The reaction mixture was allowed to stand at the ordinary temperature for two to three hours to complete the reaction. A solid (XI) separated at this stage which was filtered and crystallised from water, m.p. 93°-94°. This is soluble in dilute acid

and dilute caustic alkali but insoluble in dilute ammonia. (Found: N, 11·77. $C_{10}H_{10}O_2N_2S$ requires N, 12·10 per cent.).

Through the filtrate from compound (XI) steam was passed for three to four hours to remove some oily matter ; on cooling a solid (XIII) separated which was soluble in dilute alkali but insoluble in dilute acid and even in strong acid. It was crystallised from alcohol, m.p. 306°. (Found: N, 21·20. $C_7H_6ON_2$ requires N, 20·89 per cent.). The compound possesses identical properties as phenylene urea (m.p. 305°-307°).

The reaction of *o*-phenylene diamine with the ester was also conducted at the ordinary temperature without using any solvent. A solid separated during the course of reaction. The mixture was shaken with dilute hydrochloric acid to remove the excess of *o*-phenylene diamine. The solid portion insoluble in hydrochloric acid (XII) was filtered, washed and crystallised from dilute alcohol ; m.p. 122°-123°. The compound (XII) is soluble in dilute alkali. (Found: N, 11·83. $C_{10}H_{10}O_2N_2S$ requires N, 12·10 per cent.).

To the filtrate from (XII) dilute ammonia was added when a precipitate was obtained. This substance on crystallisation from water melted at 93° and was found to be identical with compound (XI).

Action of Potassium hydroxide upon (XI).

N-carbothoxy-*o*-phenylene thiourea was heated with the alkali solution (20%) for half an hour under reflux. The solution was then allowed to cool and acidified with dilute hydrochloric acid when a precipitate was obtained. This was filtered, washed with water and crystallised from dilute alcohol, m.p. 301°-302°. It gives a disulphide with iodine which melts at 230°. The compound has got all the properties common with phenylene thiourea. The melting point of phenylene thiourea is given in Richter's book as 298° and in Meyer and Jacobson it is 292°-293°. The melting point of the disulphide is given in literature to be 230°. (Found: N, 18·56. $C_7H_6N_2S$ requires N, 18·66 per cent.).

Action of Potassium hydroxide upon (XII).

N-thiocarbethoxy-*o*-phenylene urea was heated with the potassium hydroxide solution (20%) for half an hour. The solution was then allowed to cool and acidified with dilute hydrochloric acid.

During the addition of acid sulphuretted hydrogen was evolved and a white precipitate mixed with sulphur was obtained. This was freed from sulphur by warming with alcohol when it went into solution leaving the sulphur insoluble. On concentration of the alcoholic solution a crystalline compound (m.p. 305°) was obtained. It was purified by crystallisation from dilute alcohol. It has got all its properties common with phenylene urea. (Found: N, 20·68. $C_7H_6N_2O$ requires N, 20·89 per cent.)

Action of 1:2-*Naphthylene diamine on Diethylxanthic formic ester*: *Formation of* (*XIV*) *and* (*XV*).

1:2-Naphthylene diamine (1·5 g.) was added to the ester (2 g.) under ice cooling. The reaction took place with evolution of heat and hydrogen sulphide. After fifteen minutes the mixture was diluted with alcohol and allowed to stand at the ordinary temperature for three to four hours to complete the reaction during which a solid substance gradually accumulated which was filtered and crystallised from pyridine ; m.p. 250.° It is perfectly insoluble in both dilute acid and dilute alkali. It is not desulphurised when heated with freshly prepared yellow mercuric oxide. (Found: N, 12·21 ; S, 13·62. $C_{12}H_6ON_2S$ requires N, 12·38 and S, 14·15 per cent.). The filtrate from (XIV) was evaporated to dryness when a small quantity of the same substance was obtained.

The action of naphthylene diamine on the ester was tried again at a higher temperature. The reaction, as before, was first of all carried under ice cooling in alcoholic suspension ; and after an hour the mixture was heated under reflux for two hours when the reaction was completed. The solution was then cooled and the solid (XV) formed was filtered and crystallised from pyridine. The substance is soluble in no other ordinary organic solvents. It is perfectly insoluble in dilute acid and alkali ; m.p. 304°. (Found: N, 13·52. $C_{25}H_{18}O_3N_4$ requires N, 13·27 per cent).

Ethylenemonothio-diurethane (*XVI*) *and Ethylene thiourea* (*XVII*).

To an alcoholic solution of the ester (8 g.) ethylene diamine (2·4 g.) was gradually added under ice cooling ; the reaction took place at once with the evolution of heat and liberation of hydrogen sulphide. The reaction mixture was allowed to stand for two to three hours to complete the reaction. The solution was then diluted with water when an oil separated out. The dilute solution was

shaken with hydrochloric acid to remove the excess of ethylene diamine. At this stage the oil solidified. The solid (XVI) was separated by filtration and crystallised from dilute alcohol, m.p. 110°-111°. It is insoluble in dilute acid and dilute alkali. (Found: N, 12·56. $C_8H_{16}O_3N_2S$ requires N, 12·72 per cent.).

To the acid filtrate from (XVI) dilute ammonia was added as in the case of the reaction with *o*-phenylene diamine but in this case nothing could be obtained.

The action of ethylene diamine on the ester was carried out under different conditions. In this case no solvent was used and the reaction was conducted at the ordinary temperature. The solid (XVII) which separated from the reaction mixture was filtered from the oily part and crystallised from dilute alcohol ; m.p. 193°-194°. It is soluble in alkali but could be precipitated with dilute acid. It forms a mercaptide, a disulphide and a lead salt with mercuric chloride, iodine and lead acetate respectively. It gives a hydrochloride melting at 304°-305°. (Found: N, 27·22. $C_3H_6N_2S$ requires N, 27·45 per cent.).

To the oily filtrate from (XVII) dilute alcohol was added when it readily passed into solution which, on being diluted with water, yielded a solid substance. It was filtered and crystallised from alcohol, m.p. 110°-111°. This compou nd on examination was found to be identical with compound (XVI).

Action of Hydrochloric Acid upon Ethylene monothio-diurethane.

Ethylene monothio-diurethane was heated under reflux with concentrated hydrochloric acid for half an hour when a clear solution was obtained, which on being cooled yielded no solid product. A small portion of the solution after neutralisation with alkali was found to yield no solid product. So the acid solution was diluted with water and evaporated to dryness on the water-bath when a crystalline residue was left behind which was found to be very soluble in water, alcohol and acetone. It was therefore, washed with ether (in which it is almost insoluble) to remove any tarry matter adhering to it. The substance gives test for halogen, decomposes bicarbonate of sodium. The substance was kept in a caustic potash desiccator for twenty-four hours to remove any adhering hydrochloric acid ; for it was suspected that it decomposed the bicarbonate owing to some acid adhering to it but it was afterwards found that a hydrochloride of the compound was formed. In order to isolate the

free base it was dissolved in the least amount of water and then sodium acetate added when a solid was obtained.* This on being crystallised from dilute alcohol melted at 193°, identical with compound (XVII).

Action of Potassium hydroxide on Ethylene-monothiodiurethane.

Ethylene monothiodiurethane was mixed with the caustic potash solution (20%) and allowed to stand at the ordinary temperature for twenty-four hours. It was then heated at 60-70° under reflux for two hours when a clear solution was obtained. The solution was then allowed to cool and acidified with dilute hydrochloric acid when hydrogen sulphide was evolved and a small quantity of sulphur separated. The solution was filtered from sulphur and the filtrate evaporated to dryness. The solid residue was extracted with absolute alcohol and from the alcoholic solution on cooling the ethylene thicurea was obtained on dilution with water.

Semicarbazide monothiocarboxylic ester (XVIII).

Semicarbazide hydrochloride (4·5g.) dissolved in the least quantity of water was treated with anhydrous sodium carbonate (2 g.) to liberate the free base. The volume of the solution was then increased by the addition of alcohol and then added to the required quantity of the ester. Reaction began in the cold with evolution of some heat and hydrogen sulphide. The mixture was allowed to stand for about two hours at the ordinary temperature and then heated under reflux for half an hour to complete the reaction. On allowing to stand overnight needle-shaped crystals were found to have been formed in the solution which after filtration were crystallised from water, m.p. 161°. It is soluble in dilute acid and dilute alkali. On being boiled with strong hydrochloric acid it is decomposed into alcohol, carbon oxysulphide and semicarbazide hydrochloride. (Found: N, 26·20. $C_4H_9O_2N_3S$ requires N, 25·76 per cent.).

Thiosemicarbazide carboxylic ester (XIX).—An alcoholic solution of the ester (2 g.) and thiosemicarbazide (2 g.) were heated for an hour under reflux when a clear solution was obtained. Hydrogen sulphide was evolved during the reaction. On allowing the solution to cool a solid separated which after filtration was crystallised from

* The free base can also be isolated by boiling with alcohol.

water, m.p. 155°-156°. The substance is soluble in dilute alkali but insoluble in dilute acid. (Found: N, 25·86. $C_4H_9O_2N_3S$ requires N, 25·76 per cent.).

The filtrate from (XIX) was evaporated to dryness and a second crop of the same substance was obtained.

Action of Hydrochloric Acid on Thiosemicarbazide carboxylic ester: Formation of (XXIII).—Thiosemicarbazide carboxylic ester was heated with strong hydrochloric acid for half an hour when it passed into solution. The solution after being diluted with water was evaporated to dryness. The white crystalline solid (XXIII) thus obtained was recrystallised from water. It shrinks at 179° and melts at 189°. The substance is free from chlorine and liberates carbon-dioxide from sodium bicarbonate. Though it contains sulphur it does not give a mercaptide or a disulphide with mercuric chloride and iodine respectively. It is not desulphurised when boiled with freshly prepared yellow mercuric oxide. So the sulphur atom is present in the ring. It gives a benzylidene derivative which melts at 158°-159°. (Found: N, 24·89. $C_3H_3O_3N_3S$ requires N, 25·40 per cent.).

4-Phenylthiosemicarbazide ethylcarbonic ester (XX).—To 2 gms. of the ester, 4-phenylthiosemicarbazide (3·5 gms.) was added. The reaction took place even at the ordinary temperature with the evolution of heat and hydrogen sulphide. After allowing the mixture to stand for two hours it was diluted with alcohol and then heated under reflux for about half an hour. The separated solid was filtered and crystallised from alcohol; m.p. 149°—150°. It is soluble in dilute alkali and can be precipitated by means of dilute acid. (Found: N,17·23; S, 12·85. $C_{10}H_{13}O_2N_3S$ requires N, 17·57; S, 13·38 per cent.).

4-para Tolylthiosemicarbazide ethylcarbonic ester (XXI).—In a manner similar to the preceding reaction *p*-tolyl-thiosemicarbazide was condensed with the ester. The product was crystallised from a mixture of pyridine and water; m.p. 183°—184°. It is insoluble in dilute acid but soluble in alkali. (Found: N, 16·74. $C_{11}H_{15}O_2N_3S$ requires N, 16·53 per cent.).

β-Naphthylthiosemicarbazide ethylcarbonic ester (XXII) was obtained in a similar manner form β-naphthylthiosemicarbazide (4 g.) and the ester (2 g.). The product was crystallised from pyridine; m.p. 287°-288°. It is soluble in alkali but can be precipitated with acid. (Found: N, 14·71. $C_{14}H_{15}O_2N_3S$ requires N, 14·52 per cent.).

Benzidine-monothiodicarbonic ester (XXIV).—An alcoholic solution of the ester (2 g.) was added to benzidine (2 g.) under ice cooling. The reaction took place with liberation of heat and hydrogen sulphide. The reaction mixture was allowed to stand at the ordinary temperature for two to three hours and then heated under reflux for half an hour more to complete the reaction. The solid product obtained on cooling the solution was filtered and crystallised from acetic acid. The filtrate on evaporation gave a second crop of the same substance, m.p. 211°-212°. It is soluble in dilute alkali but insoluble in dilute acid. (Found: N, 8·41. $C_{18}H_{20}O_3N_2S$ requires N, 8·13 per cent.).

Tolidine-monothiodicarbonic ester (XXV) was obtained and purified as in the previous case ; m.p. 125°-26°. The substance is soluble in alkali but insoluble in acid. (Found: N, 7·61. $C_{20}H_{24}O_3N_2S$ requires N, 7·52 per cent.).

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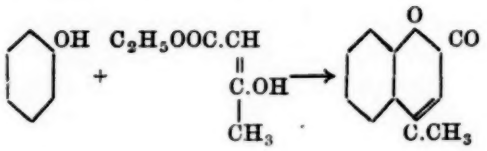
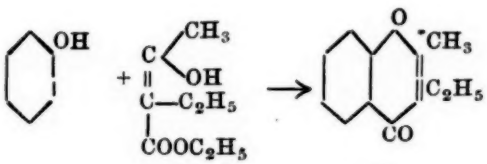
Studies in Coumarin Condensations. Part I. The Condensation of Allylacetoacetic Ester with Phenols.

By Kuverji Gosai Naik, Ranchhodji Dajibhai Desai and Haribhai Ranchhodji Desai.

Though ethyl acetoacetate condenses with phenols to give coumarins (I)* Simonis and his co-workers have shewn that ethylacetoacetic ester condenses with phenols in presence of phosphorous pentoxide to form benzo-γ-pyrones (II):



(I)



(II)

According to Ghosh and Jacobson (*J. Chem. Soc.*, 1915, **107**, 424, 959, 1051), the formation of either the benzo-α-pyrones (coumarins) or the benzo-γ-pyrones mainly depends upon the character of the radical present in the substituted acetoacetic esters, whereas the condensing agent plays a subsidiary part. Thus, even using concentrated sulphuric acid as the condensing agent, the acetoacetic esters of the general formula, $CH_3.C(OH)=CR.COOC_2H_5$ give the benzo-γ-pyrones, where R is the benzyl or phenyl group. If R is

* Pechmann, *Ber.*, 1884, **17**, 929, 1646, 2187; 1899, **32**, 3681; 1901, **34**, 423; Fries and Klostermann, *Annalen*, 1908, **3621**; Simonis, *Ber.*, 1913, **46**, 2014; 1914, **47**, 2229).

ethyl, a mixture of α- and γ-pyrones is obtained, while only coumarins are obtained if R is either hydrogen or methyl. This work of Ghosh and Jacobson has been contradicted by Baker (*J. Chem. Soc.*, 1925, **127**, 2349) and Baker and Robinson (*J. Chem. Soc.*, 1926, **129**, 1981) and they are of opinion that all the products prepared by Ghosh and Jacobson are benzo-α-pyrones and not benzo-γ-pyrones. Thus the available views regarding the influence of the radical present in the methylene group of the acetoacetic ester are conflicting.

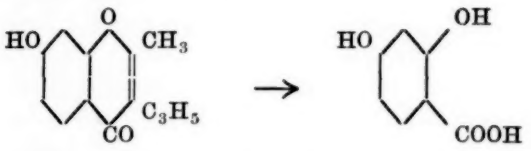
On consulting the literature, it was found that the effect of an alkyl radical containing more than two carbon atoms, such as propyl, butyl, etc. and an unsaturated alkyl radical, such as allyl, substituted in place of one of the hydrogens in the methylene group of the acetoacetic ester, on the course of the reaction between the phenols and such esters, has not been fully and systematically studied. This communication describes the results of the condensation of various phenols with allyl acetoacetic ester, using concentrated sulphuric acid as the condensing agent.

Phenol, resorcinol, pyrogallol, *m*-cresol, α-naphthol, β-naphthol, phloroglucinol, guaiacol, thymol, catechol, and quinol were condensed with the above ester. Phenol, however, failed to give any solid product; α-naphthol condensed very easily giving almost a quantitative yield of 4-methyl-3-allyl-5 : 6-naphtho-pyrone. The phenols, having a substituent in the *meta*-position, *e.g.*, resorcinol, *m*-cresol, and phloroglucinol condensed very readily giving almost quantitative yields of the corresponding coumarins. Pyrogallol condensed with the ester giving the α-pyrone when phosphorous oxychloride was used as the condensing agent. Catechol, guaiacol, thymol, β-naphthol and quinol did not condense at all.

The condensation of resorcinol with the ester was also carried out using gaseous hydrochloric acid as the condensing agent. The reaction proceeded very readily in the cold , and a product containing chlorine was obtained. The acetyl and benzoyl derivatives also contain chlorine. The constitution 7-hydroxy-3-chloropropyl-4-methyl-benzo-α-pyrone has been provisionally assigned to this compound.

When coumarins, obtained from resorcinol and α-naphthol, were subjected to the action of 50% boiling aqueous solution of sodium hydroxide (4 hours), and the solution was acidified, the original products were obtained in each case. If the products were

benzo-γ-pyrones, resorcylic acid and naphthol-carboxylic acid respectively would result:



The benzo-γ-pyrones are known to give the hydroxy carboxylic acids on hydrolysis (Ghosh and Jacobson, *loc. cit.*), but the α-pyrones may or may not give them. As the carboxylic acids were not obtained in the present case, the α-pyrone constitution has been suggested for them.

Experimental.

7-Hydroxy-3-allyl-4-methyl-benzo-α-pyrone.—To a mixture of resorcinol (2 g.) and allylaceto-acetic ester (3 g.) concentrated H_2SO_4 (20 g.) was added in small amounts. It was found necessary to keep the mixture cool. It was kept overnight and then poured into a large amount of water. A pale-brown solid separated, which was filtered off and dried (yield, 3·8 gms.) When the crude substance was boiled with alcohol, it became white, and melted at 221°-222°. It is sparingly soluble in alcohol and glacial acetic acid. It was recrystallised from a mixture of pyridine and water, when it was obtained in small white needles. The substance for analysis was dried in an air-oven at 120°. (Found: C, 72·09; H, 5·79. $C_{13}H_{12}O_3$ requires C, 72·22; H, 5·55 per cent.)

The *acetyl derivative* was prepared by boiling the substance with acetic anhydride for an hour. When crystallised from alcohol, white plates melting at 152°-153° were obtained. (Found: C, 74·88; H, 4·89. $C_{20}H_{16}O_4$ requires C, 75·0 and H, 5·0 per cent.)

Hydrolysis of 7-Hydroxy-3-allyl-4-methyl-benzo-α-pyrone.—The substance (1 g.) was boiled with 15 c. c. of 50% aqueous caustic potash for four hours. The clear solution was acidified with HCl and the product that separated, was crystallised from pyridine and water. It was found to be the original substance, as was apparent from its m. p. and its acetyl derivative.

7-Hydroxy-3-chloropropyl-4-methyl-benzo-α-pyrone. — Resorcinol (2 g.) and allylacetoacetic ester (3 g.) were dissolved in 10 c. c. of

glacial acetic acid. Dry gaseous hydrogen chloride was passed into the mixture for two hours. As the mixture became hot, the flask had to be cooled under water. After an hour, the mixture became viscid, and on keeping overnight, white crystalline plates separated out. On diluting the mixture with water, more of the substance separated (yield, 4 gms.). The product which crystallised from alcohol in white, prismatic needles, melted at 200°-201°. The chlorine in it was not removed even by boiling its alcoholic solution with sodium acetate solution. (Found: Cl, 14·05. $C_{13}H_{13}O_3Cl$ requires Cl, 14·06 per cent.)

The *acetyl derivative* prepared as above, crystallised from alcohol in white, short needles melting at 122°-123°. (Found: Cl, 12·28. $C_{16}H_{15}O_4Cl$ requires Cl, 12·05 per cent.)

The *benzoyl derivative* crystallised from glacial acetic acid in white, shining needles melting at 183°. (Found: Cl, 10·15. $C_{20}H_{17}O_4Cl$ requires Cl, 9·96 per cent.)

3-*Allyl*-4-*methyl*-5 : 6-*naphtho*-α-*pyrone*.—A mixture of α-naphthol (2 g.) and allylacetoacetic ester (2 g.) was treated with concentrated H_2SO_4 (20 g.). After keeping the mixture overnight, it was poured into water (yield, 3 gms.). After treatment with animal charcoal in alcoholic solution the substance was obtained as yellowish white plates, m. p. 155°-156°. (Found: C, 81·33 ; H, 5·65. $C_{17}H_{14}O_2$ requires C, 81·6 ; H, 5·6 per cent.)

3-*Allyl*-4 : 7-*dimethyl*-*benzo*-α-*pyrone*.—This was prepared as usual from *m*-cresol (3 g.) allylaceto-acetic ester (3 g.) and concentrated H_2SO_4 (10 gm.) (yield, 3·2 gms). Recrystallisation from alcohol gave yellowish white plates, m. p. 126°-127°. (Found: C, 78·24; H, 6·65. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·54 per cent.)

5 : 7-*Dihydroxy*-3-*allyl*-4-*methyl*-*benzo*-α-*pyrone*.—This was prepared in a manner similar to the above, from anhydrous phloroglucinol (1·5 g.), allyl acetoacetic ester (1·5 g.) and concentrated H_2SO_4 (10 gm.) (yield, 2 gms.). The pale yellow powder was recrystallised from dilute acetic acid, when pale brown, silky needles, m. p. 207°-208° were obtained. It is very soluble in alcohol, acetone and glacial acetic acid, but sparingly soluble in benzene and petroleum. (Found: C, 66·75 ; H, 5·50. $C_{13}H_{12}O_4$ requires C, 67·24 and H, 5·17 per cent.)

The *acetyl derivative* crystallises from alcohol in white plates, m. p. 130°-131°. (Found: C, 64·25; H, 5·61. $C_{17}H_{16}O_6$ requires C, 64·56; H, 5·28 per cent.)

7 : 8-*Dihydroxy*-3-*allyl*-4-*methyl*-*benzo*-α-*pyrone*.—This could not be obtained by using H_2SO_4 as a condensing agent. A mixture of pyrogallol (2 g.), allylacetoacetic ester (2 g.) and phosphorous oxychloride (1·5 g) was heated on a water-bath for nearly an hour. Copious fumes of hydrogen chloride were evolved. After the reaction was over, the viscous mass was poured into water. Recrystallisation from diiute acetic acid gave white, small plates melting at 175°-176° (yield, 2·5 gm). (Found : C, 66·87 ; H, 5·23. $C_{13}H_{12}O_4$ requires C, 67·24 ; H, 5·17 per cent.)

The *acetyl derivative* crystallises from alcohol in white, prismatic needles, m. p. 145°-146°. (Found : C, 64·12 ; H, 5·51. $C_{17}H_{16}O_6$ requires C, 64·56 ; H, 5·28 per cent.)

We desire to express our gratitude to the Government of His Highness the Maharaja Gaekwar, for a grant which has defrayed the expenses incurred in this research.

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On the Inhibiting Action of Sucrose on Taurocholate, Saponin and Oleate Hemolysis.

By A. C. Roy and K. C. Sen.

In a previous paper in this *Journal* (Sen and Sen, 1928, **5**, 261) we have shown that sucrose has an inhibiting action on the taurocholate hemolysis of sheep's red blood corpuscles. It was shown that when taurocholate was used in saline, less of the substance was necessary to effect a complete hemolysis of a fixed amount of red blood corpuscles than when all the solutions were prepared in sucrose solutions. In a very recent paper Ponder and Yeager (*Biochem. J.*, 1928, **22**, 703) have independently come to the conclusion that glucose, sucrose and lactose have an inhibit in effect on taurocholate hemolysis of human erythrocytes. This investigation thus confirms the results obtained by us. We have also discussed in another previous paper, the mechanism of the inhibition of saponin hemolysis in presence of sugar (*cf.* Sen and Basu, this *Journal*, 1928, **5**, 1). In view of the fact that no comparative study of the inhibiting action of sugar has been made on taurocholate, saponin and oleate hemolysis, it was decided to make some experiments on these three hemolytic systems in presence of sucrose, and in this note, we desire to present the data of the time-dilution curves of these three hemolytes both in isotonic saline as well as in isotonic sucrose.

As far as it appears to us, the effect of sucrose on oleate hemolysis has not been investigated previously.

Experimental.

The method of experimentation is almost the same as described in previous papers. In order to have comparable data on the hemolysis in the two different solutions, the same sample of red blood corpuscles has been used. One portion of the freshly defibrinated corpuscles of sheep was washed by centrifuging three times with an isotonic saline ; these corpuscles were then suspended in normal saline to give a concentration of one per cent. Another portion of the same fresh corpuscles was treated similarly with an isotonic sucrose solution and then this portion was suspended in isotonic sugar solution to give a concentration of one per cent.

The actual hemolytic experiments with the two different suspensions were carried out side by side in order to avoid any change in the nature of the corpuscles such as by ageing or in the nature of the hemolytes themselves. The total volume in every case was five c.c. and in the series of experiments the total volumes were adjusted to the definite standard by using either an isotonic saline or an isotonic sugar as the case may be. In this way perfectly comparative results could be obtained. In the concentrations studied in this paper, the end-point in the hemolysis was very sharp and could be detected within an error of two seconds only. The solutions of taurocholate, saponin and potassium oleate were prepared only fifteen minutes before the actual experiments in each case were made. The amount of corpuscles taken in every case was one c.c. of the one per cent. suspension prepared before. In the following three tables the results are shown.

The concentration of taurocholate was 0·3 per cent. and the saponin and oleate concentrations used were 1 in 1,000 and 1 in 10,000 respectively.

TABLE I.

Taurocholate hemolysis.

Amount of taurocholate in c.c.	Final concentration.	Time of complete hemolysis. In isotonic saline.	In isotonic sucrose.
0·4	1/4166	11 mins. 32 secs.	26 mins. 58 secs.
0·5	1/3333	6 ,, 8 ,,	24 ,, 55 ,,
0·6	1/2777	4 ,, 0 ,,	20 ,, 40 ,,
0·7	1/2381	1 ,, 51 ,,	16 ,, 35 ,,
0·8	1/2083	1 ,, 39 ,,	15 ,, 39 ,,

TABLE II.

Saponin hemolysis.

Amount of saponin in c.c.	Final concentration.	Time of complete hemolysis. In isotonic saline.	In isotonic sucrose.
0·2	1/25,000	21 mins. 16 secs.	52 mins. 37 secs.
0·3	1/16,666	10 ,, 38 ,,	17 ,, 54 ,,
0·4	1/12,500	6 ,, 27 ,,	14 ,, 40 ,,
0·5	1/60,000	2 ,, 57 ,,	12 ,, 17 ,,
0·6	1/8333	2 ,, 6 ,,	8 ,, 25 ,,

TABLE III.

Oleate hemolysis.

Amount of oleate in c.c.	Final concentration.	Time of complete hemolysis. In isotonic saline.	In isotonic sucrose.
0·5	1/100,000	13 mins. 50 secs.	19 mins. 31 secs.
0·6	1/83,333	8 ,, 1 ,,	15 ,, 54 ,,
0·8	1/62,500	2 ,, 45 ,,	13 ,, 5 ,,
1·0	1/50,000	1 ,, 40 ,,	11 ,, 2 ,,

Discussion.

From a perusal of the above tables it will be immediately observed that in every case a considerable inhibition of hemolysis is obtained. A very interesting point here is that the time-dilution curves of these hemolytic systems in both saline and isotonic sucrose are normal. In a recently communicated paper, we have shown that there is some abnormality in taurocholate hemolysis when higher concentrations of the hemolyte and corpuscles are used in saline but when the concetrations are low, no peculiarity in the time-dilution curve is to be noticed. It is to be noted in these results that with a low concentration of corpuscles and hemolyte, there is no abnormality in the time-dilution curve of taurocholate hemolysis when experiments are carried out in isotonic sugar solution. Experiments are being carried out with higher concentrations of taurocholate and corpuscles in sugar solutions to see if any abnormality in the time-dilution curve can be obtained or not as was the case in saline. In some preliminary experiments, some abnormalities have actually been observed but we are not in a position to confirm those data as yet.

When a comparative study of the hemolytic efficiency of the different hemolytes studied in this paper is made, it is observed that under the experimental conditions, oleate has the highest hemolytic power, then comes saponin while taurocholate has the lowest hemolytic power amongst the three. This is evident from the extremely low concentration in which oleate and saponin have been used. When we come to the question of the inhibiting action of sugar on the hemolytic efficiency of these three hemolytes, it is quite natural that sugar should have a greater effect on taurocholate hemolysis than that of the other two. If we also calculate the final concentrations of saponin and oleate and take into consideration the fact that

the oleate concentration is usually one-tenth of that of saponin, we come to the conclusion that sugar has also a greater inhibiting action on saponin than on oleate. It thus appears that oleate is the least influenced by sugar ; it must be stated at this place however, that this comparison is not very exact, because the three hemolytes had to be usedin widely different concentrations and the time of hemolysis is not a linear function of the hemolyte concentration. In a previous paper we have discussed the mechanism of the inhibiting action of sugar on hemolysis, It was suggested there that the action of sugar is on the membrane of the red-blood corpuscles and an analogy was drawn between the action of sugars on red blood corpuscles and that on a copper-ferrocyanide membrane. Ponder and Yeager (*loc. cit.*) have shown in their recent paper that there is practically no action between sugar and taurocholate but the effect of sugar in producing the inhibition in hemolysis is really on the red-blood corpuscles themselves. This confirms our suggestion in a general way but the actual mechanism of how the sugar changes the nature of the corpuscle membrane is yet obscure. We are making a detailed study of hemolysis in sugar solutions and further discussion on the mechanism of inhibition by sugars will be made in future communications.

Summary.

(1) An experimental study has been made of the hemolysis of sheep's red-blood corpuscles both in isotonic saline as well as in isotonic sucrose solutions.

(2) It has been found that in both these solutions, oleate has the highest hemolytic power, then comes saponin and taurocholate has the least hemolytic power amongst the three.

(3) It has been observed that sugar has a great inhibiting action on saponin, oleate and taurocholate hemolysis. It appears also that the inhibiting action is greatest in the case of taurocholate, less in the case of saponin and least in the case of oleate when the concentrations of hemolytes are considered to be almost equal. In actual experiments, the concentrations of the hemolytes had however to be used in widely different amounts and as such the comparison of the inhibiting power of sucrose on these three hemolytes is not very exact.

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Dyes derived from Acenaphthenequinone: Acenaphthiminazoles and Acenaphthoxazoles.

By Anukul Chandra Sircar and Nirmal Chandra Guha-Ray.

Sircar and Guha (*J. Chem. Soc.*, 1924, **125**, 335) have shown that the tinctorial properties of the azine and azonium derivatives obtained from acenaphthenequinone are in no way inferior to those of the corresponding phenanthraquinone derivatives. Further Sircar and Sircar (*J. Chem. Soc.*, 1923, **123**, 1559) showed that many of the phenanthraiminazoles obtained by the condensation of substituted phenanthraquinones with various aromatic aldehydes in presence of ammonia, possess well developed tinctorial properties. In view of these observations it was natural to expect that if similar iminazole derivatives could be prepared from acenaphthenequinone and its substituted products, they would also be deep coloured and adapted for dyeing. With this object in view the present investigation was undertaken.

It has now been found that in its behaviour towards aromatic aldehydes in presence of ammonia, acenaphthenequinone does not always behave in the same way as phenanthraquinone does. Following the methods adopted by Sircar and Sircar (*loc. cit.*) for the preparation of phenanthraiminazoles, it has been found that under the same experimental conditions, with certain aldehydes acenaphthenequinone forms iminazoles, whilst with others it forms oxazoles. That aromatic aldehydes can be made to react with phenanthraquinone and ammonia, under different experimental conditions, to yield either an oxazole or an iminazole, has been shown by Sircar and Guha-Ray (*J. Chem. Soc.*, 1925, **127**, 1048) and that acenaphthenequinone in some of its behaviour differs form other cyclic diketones (*e. g.*, phenanthraquinone) has already been observed by Francesconi and Pirazzoli (*Gazzetta*, 1903, **33**, I, 36 ; *J. Chem. Soc.*, 1903, **84**, *i*, 500).*

* Compare also Japp and Streatfield (*J. Chem. Soc.*, 1882, **41**, 127) for the formation of iminazoles and oxazoles by the action of aldehydes on phenanthraquinone in presence of ammonia.

Amino- or hydroxy-acenaphthenequinones are not known. Acenaphthenequinone, and its 3-nitro- † and 3:4-dinitro-derivatives (Rowe and Davies, *J. Chem. Soc.*, 1920, **117**, 1349) only were utilised in the present investigation. The following new compounds have been prepared and their properties studied:—

(1) 2-Phenyl-acenaphthiminazole.
(2) 3′-Nitro-2-phenyl-acenaphthiminazole.
(3) 2′-Hydroxy-2-phenyl-acenaphthiminazole.
(4) 4′-Methoxy-2-phenyl-acenaphthiminazole.
(5) 3′-Methoxy-4′-hydroxy-2-phenyl-acenaphthiminazole.
(6) 4′-Chloro-2-phenyl-acenaphthiminazole.
(7) 3 : 4-Dinitro-2′-hydroxy-5′-bromo-2-phenyl-acenaphtiminazole.
(8) 3 : 4-Dinitro-4′-methoxy-2-phenyl-acenaphthiminazole.
(9) 3-Nitro-2′-hydroxy-2-phenyl-acenaphthiminazole.
(10) 3-Nitro-2′-methoxy-4′-hydroxy-2-phenyl-acenaphthiminazole.
(11) 2′-Nitro-2-phenyl-acenaphthoxazole.
(12) 4′-Dimethylamino-2-phenyl-acenaphthoxazole.
(13) 3 : 4-Dinitro-3′ : 5′-dioxy-2-phenyl-acenaphthoxazole.
(14) 3 : 4-Dinitro-3′-nitro-2-phenyl-acenaphthoxazole.
(15) 3′ : 5′-Dihydroxy-2-phenyl-acenaphthoxazole.
(16) 3-Nitro-3′ : 5′-dihydroxy-2-phenyl-acenaphthoxazole.

These iminazoles and oxazoles are coloured bodies and fairly adapted for dyeing on wool upon which they yield even shades of orange yellow to chocolate brown colour from an acid bath. They are stable substances of high melting points and give characteristic colour reactions with concentrated sulphuric acid. Unlike the phenanthraiminazoles (Sircar and Sircar, *loc. cit.*) most of them are not completely insoluble in the commoner organic solvents. Acenaphthiminazoles seem to excell the phenanthraiminazoles in their tinctorial power. Whilst the iminazoles obtained from phenanthraquinone itself are either colourless or pale yellow, those obtained from acenaphthenequinone are coloured orange yellow to bright red.

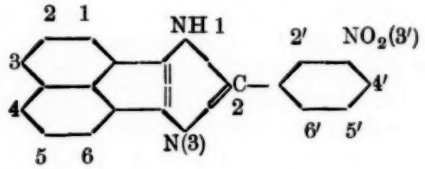
In ordinary process of dyeing from acid bath, it is found that the absorption of the dye by the fibre is very slow and the shade is not at all satisfactory. Much better results can be obtained by freshly precipitating the substance (the dye) from concentrated

† The mono-nitro-acenaphthenequinone used was prepared according to the directions given by Mayer and Kauffmann (*Ber.*, 1920, **53**, 296). It melted at 200°. Repeated attempts to prepare 3-nitro-acenaphthenequinone of m.p. 218° by following the method of Rowe and Davies (*loc. cit.*) were unsuccessful (*cf.* Sircar and Guha, *loc. cit.*).

sulphuric acid solution by addition of water. The freshly precipitated flocculent mass, after being filtered and washed, is best adapted for dyeing.

Experimental.

3′-Nitro-2-phenyl-acenaphthiminazole.



Acenaphthenequinone (1 g.) was thoroughlymixed with of *m*-nitrobenzaldehyde (1·2 g.) and dissolved in 20 c.c. of boiling amyl alcohol. Dry ammonia gas was then passed through the hot solution for about two hours. The hot solution was then cooled in ice when a reddish grey solid separated. It was filtered off, washed with ether, dried and finally crystallised from alcohol in orange coloured needles. The substance does not melt but gets discoloured from 220° and upwards. It dissolves in concentrated sulphuric acid with a reddish-brown colouration. It is soluble in alcohol, nitrobenzene, pyridine, acetic acid or acetone, insoluble in ether and slightly soluble in benzene or warm dilute alkali. It dyes chrome-mordanted and unmordanted wool to orange-yellow shades from an acid bath. (Found: N, 13·36. $C_{19}H_{11}O_2N_3$ requires N, 13·42 per cent.).

The following acenaphthiminazoles were prepared in the same way as the preceding compound.

2-Phenyl-acenaphthiminazoles—shining dark red needles mixed with rhombic plates. It does not melt below 290° and dissolves in strong sulphuric acid with a blood red colour and a reddish-violet fluorescence. It is sparingly soluble in alcohol, but more soluble in acetic acid, acetone, benzene, nitrobenzene or pyridine. It dyes red shades on wool from an acid bath. (Found: N, 10·2. $C_{19}H_{12}N_2$ requires N, 10·4 per cent.).

2′-Hydroxy-2-phenyl-acenaphthiminazole,—shining yellow rhombic plates (from pyridine). It melts with decomposition at 268° and dissolves in warm dilute alkali or strong sulphuric acid with a yellow colour. It is highly soluble in nitro-benzene or pyridine,

slightly soluble in acetic acid or acetone and insoluble in benzene. (Found: N, 10·12. $C_{19}H_{12}ON_2$ requires N, 9·86 per cent.).

4'-Methoxy 2-phenyl-acenaphthiminazole,—shining red needles melting at 268°. It dissolves in concentrated sulphuric acid with a deep red colouration. It is readily soluble in pyridine, nitro-benzene, acetic acid, acetone or benzene, but slightly soluble in alcohol. (Found: N, 9·40. $C_{20}H_{14}ON_2$ requires N, 9·39 per cent.).

3'-Methoxy-4'-hydroxy-2-phenyl-acenaphthiminazole,—minute rose-coloured needles (from pyridine) melting at 263°. With strong sulphuric acid it gives an orange-red solution. It is readily soluble in acetic acid, pyridine or nitro-benzene and slightly soluble in acetone, alcohol or benzene. It dyes wool to a light-red shade from an acid bath. (Found: N, 8·61. $C_{20}H_{14}O_2N_2$ requires N, 8·92 per cent.).

4'-Chloro-2-phenyl-acenaphthiminazole,—rose-coloured rectangular plates (from pyridine). It melts at 264° with previous shrinking at 242°. It dissolves in strong sulphuric acid with a brownish-red colour. It is readily soluble in pyridine, acetic acid or nitro-benzene, slightly soluble in acetone or benzene and insoluble in spirit. (Found: N, 8·51. $C_{19}H_{11}N_2Cl$ requires N, 9·27 per cent.)

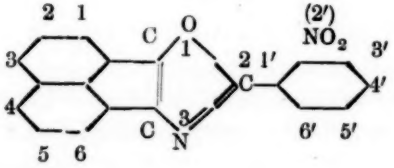
3:4-Dinitro-2'-hydroxy-5'-bromo-2-phenyl-acenaphthiminazole,—dark coloured powder (from hot pyridine solution by cautious addition of warm water). It does not melt below 290° and dissolves in strong sulphuric acid with a dark red colour. It is readily soluble in pyridine, or nitro-benzene, slightly soluble in acetic acid, alcohol or acetone and insoluble in benzene. It dyes wool to a chocolate brown shade from an acid bath. (Found: N, 12·84. $C_{19}H_9O_5N_4Br$ requires N, 12·36 per cent.).

3:4-Dinitro 4'-methoxy-2-phenyl-acenaphthiminazole is purified in a similar way to, and in properties resembles, the preceding compound. (Found: N, 13·94. $C_{20}H_{12}O_5N_4$ requires N, 14·43 per cent.).

3-Nitro-2'-hydroxy-2-phenyl-acenaphthiminazole resembles the two preceding compounds in its properties. (Found: N, 12·4. $C_{19}H_{11}O_3N_3$ requires N, 12·76 per cent.).

3-Nitro-3'-methoxy-4'-hydroxy-2-phenyl-acenaphthiminazole,—minute needles (from pyridine). It dyes wool to a light brown shade and in other properties resembles the preceding compounds. (Found: N, 12·35. $C_{20}H_{13}O_4N_3$ requires N, 11·69 per cent.).

2'-Nitro-2 phenyl-acenaphthoxazole.



Dry ammonia gas was passed through a solution of acenaphthenequinone (1 g.) and *ortho*-nitro-benzaldehyde (1·2 g.) in 60 c.c. boiling amyl alcohol. When the reaction began the mixture was cooled by freezing mixture and the current of ammonia allowed to continue for two hours. On standing for five days a buff-coloured precipitate was found to have separated. It was purified by precipitation from pyridine solution by cautious addition of warm water and obtained in a partly crystalline and partly amorphous form.

It is orange red in colour, shrinks at 263° but does not melt below 290°. It dissolves in concentrated sulphuric acid with a dark red colour. It is slightly soluble in alcohol, acetone or benzene and readily soluble in acetic acid, nitro-benzene or pyridine. It dyes wool to an orange yellow shade from an acid bath. (Found: N, 9·29. $C_{19}H_{10}O_3N_2$ requires N, 8·92 per cent.).

The following acenaphthoxazoles were prepared practically in the same way as the preceding compound, except that cooling was not found necessary. The separated solids were collected after twenty-four hours and any variation in the method of purification has been indicated within bracket. Their properties, except where otherwise stated, were also found to be practically the same as those of the preceding compound.

4'-Dimethylamino-2-phenyl-acenaphthoxazole,—light rose coloured rectangular plates. (Found : N, 9·04. $C_{21}H_{16}ON_2$ requires N, 8·97 per cent.).

3 : 4-Dinitro-3'-nitro-2-phenyl-acenaphthoxazole, — dark brown needles (from alcohol). It dyes wool to a dark chocolate shade. (Found : N, 13·86. $C_{19}H_8O_7N_4$ requires N, 13·86 per cent.).

3 : 4-Dinitro-3' : 5'-dihydroxy-2-phenyl-acenaphthoxazole,—chocolate coloured powder which dyes wool to a chocolate brown shade. (Found : N, 10·65. $C_{19}H_9O_7N_3$ requires N, 10·74 per cent.).

8′:5′-Dihydroxy-2-phenyl-acenaphthoxazole.—(The solid which separated was purified by repeatedly boiling with sodium bisulphite solution and filtering hot). It dyes wool to a light brown shade. (Found: N, 8·87. $C_{19}H_{11}O_3N$ requires N, 4·85 per cent.).

N. B.—The substance is extremely stable and does not decompose even on prolonged heating on a platinum foil in open flame. The low percentage of N found can be explained on the assumption that the substance did not undergo complete decomposition.

3-Nitro-3′: 5′-dihydroxy-2-phenyl-acenaphthoxazole—(purified by boiling with nitro-benzene, in which it is only slightly soluble, and filtering hot). It dyes wool to a brown shade.

N. B.—This compound like the preceding one is also extremely stable and the combustion results were far from being satisfactory.

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Ring Closure of Hydrazomonothiodicarbonamides with Acetic Anhydride: Formation of Iminothiobiazolones and Iminothiol-triazoles.

By Praphulla Chandra Guha and Tarini Kanta Chakraborty.

The ring-closing action of acetic anhydride upon hydrazo-dithiodicarbonamide and its substituted derivatives has been studied by one of us (Guha, *J. Amer. Chem. Soc.*, 1923, **45**, 1036) where it has been shown that the reaction takes place with the elimination of sulphuretted hydrogen yielding 2:5-diamino-1:3:4-thiodiazoles. In the present paper, the ring-closure of the following substituted hydrazodicarbonamides with acetic anhydride has been studied of which I-VII are substituted in the thiocarbonamide groupings, VIII and IX are substituted in the carbonamide groupings, X is substituted both ways and XI is an unsubstituted dicarbonamide.

$CH_3NH.CS—NH—NH—CO—NH_2$ (I)

$C_3H_5NH—CS—NH—NH—CO—NH_2$ (II)

$C_6H_5NH—CS—NH—NH—CO—NH_2$ (III)

o-$CH_3.C_6H_4—NH—CS—NH—NH—CO—NH_2$ (IV)

p-$CH_3.C_6H_4—NH—CS—NH—NH—CO—NH_2$ (V)

$(CH_3)_2C_6H_3.NH—CS—NH—NH—CO—NH_2$ (VI)

β-$C_{10}H_7—NH—CS—NH—NH—CO—NH_2$ (VII)

$NH_2—CS—NH—NH—CO—NHPh$ (VIII)

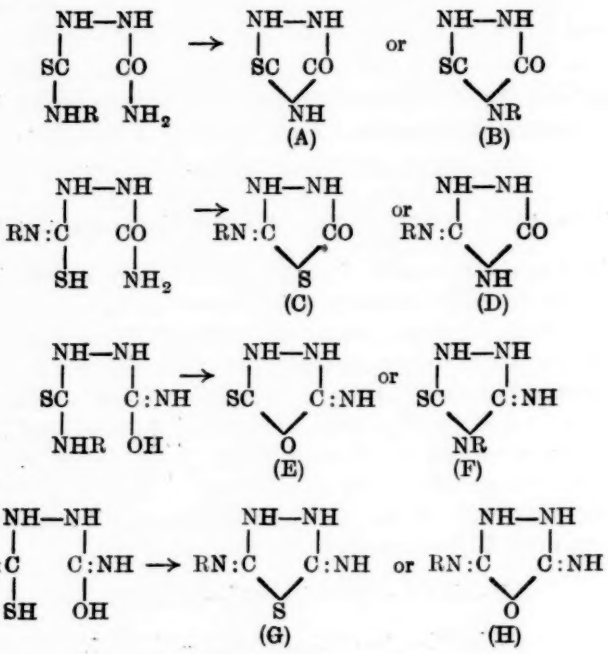
$PhNH—CS—NH—NH—CO—NH—Ph$ (IX)

$NH_2—CS—NH—NH—CO—NHC_{10}H_7(\alpha)$ (X)

$NH_2—CO—NH—NH—CO—NH_2$ (XI)

Monosubstituted hydrazo-monothio-dicarbonamides of the type $RNH—CS—NH—NH—CO—NH_2$ might react in the following four

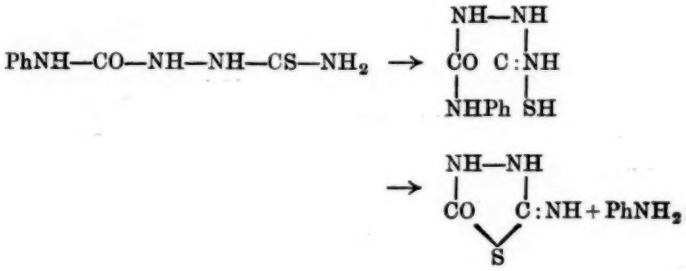
different ways to yield one or more of the ring-closed compounds of the type A to H.



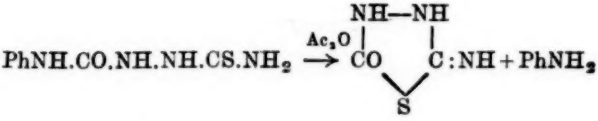
But the compounds actually isolated correspond to the general formula $C_2H_2RON_3S$ and so they cannot possess the structure as represented by formulae A, D, E, F, G or H, F and G being free of oxygen, D and H being free of sulphur, A and E being free of the group R. So the choice of formula must be made from B and C. Again the compounds possess no mercaptanic properties necessitating the rejection of formula of type B. But a formula of type C meets all the points. The acetyl derivatives of the substituted-iminothio-biazolones are invariably obtained from the hydrazide I-VI which on deacetylation give the free R-iminothiobiazolones. Besides the formation of the acetyl-R-imino-thiobiazolones, indication is given as to the formation of other products and the actual isolation of more than one product has been possible with the hydrazides II, III and V. It is worth mentioning that one of the isolable reaction products from the hydrazide V happens to be an iminothioltriazole of type F. The hydrazide VII peculiarly enough gets completely

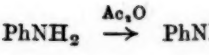
decomposed with the regeneration of β-naphthyl*iso*thiocyanate almost in a quantitative yield.

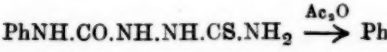
The hydrazide VIII under mild treatment gives mono- and di-acetyl derivatives of iminothiobiazolone. The ring closure is evidently effected with the elimination of aniline, thus:—

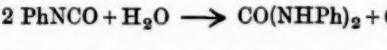


But when subjected to a more drastic treatment, *viz.*, boiling with acetic anhydride over a free flame, the hydrazide gets decomposed yielding diphenylurea, acetanilide, a trace of monoacetyliminothiobiazolone and two more compounds melting at 92-93° and 115° respectively. The formation of acetyl-iminothiobiazolone, diphenylurea and acetanilide can be explained thus:—







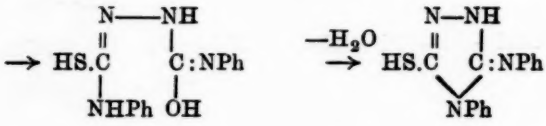


The formation of unsubstituted iminothiobiazolone in the present instance and of substituted iminothiobiazolones with the hydrazides containing substituted thiocarbonamide groupings is significant.

* The analytical values of the compound, m.p. 92-93°, agree fairly well with those of diacetyl thiosemicarbazide (Calc. N, 24·28; S, 18·5. Found: N, 24·70; S, 18·67 per cent.).

The behaviour of the sym-disubstituted hydrazide PhNH—CS—NH—NH—CO—NHPh appears to be peculiar, as instead of yielding the expected iminothiobiazolone derivatives, it gives 1-*N*-phenyl-2-phenylimino-5-thiol-dihydro-1:3:4-triazole, thus:—

PhNH—CS—NH—NH—CO—NH—Ph



When boiled with acetic anhydride, the hydrazide suffers decomposition yielding diphenylurea as the main product.

The hydrazide IX, like VII, gets easily decomposed and the α-napthyl*iso*cyanate so formed reacts readily with water to give di-α-napthylcarbazide.

Hydrazodicarbonamide (XI) is left quite unaffected even when boiled with acetic anhydride for several days, but when the mixture is heated in a sealed tube at 200° it gets decomposed into various products amongst which carbon dioxide has been identified and sym.-diacetylhydrazine isolated.

Experimental.

Hydrazo-dicarbonmonothiomethylamide (I).

Semicarbazide hydrochloride (5·6 g.) was dissolved in the least quantity of water and sodium carbonate (2·7 g.) added to it. Molecular proportion of methyl mustard oil dissolved in the least quantity of alcohol was added and the mixture was warmed. Within a minute or two the hydrazide separated out, which was crystallised from alcohol. The pure sample thus obtained melted at 212°, and the yield was quantitative. (Found: N, 37·62. $C_3H_8ON_4S$ requires N, 37·84 per cent.).

2-*Methylimino*-4-*acetyl*-5-*keto*-2:3:4:5-*tetrahydro*-1:3:4-*thiodiazole*.

The above hydrazide (5 g.) was heated with a slight excess of acetic anhydride and the hot clear solution was poured into 100-120 c.c. of cold water and the aqueous solution boiled for some time

when an oily product separated which, however, solidified after 24 hours. It was filtered, under suction, washed with ether and crystallised from alcohol. It is very slightly soluble in water and in acid; alkali decomposes it producing a faint smell of *iso*cyanide; m.p. 197°. Yield 1·5 gms. (Found: N, 24·02. $C_5H_7O_2N_3S$ requires N, 24·3 per cent.).

Hydrolysis of the above: The free basic thiodiazole compound.

Two grams of the above acetate were boiled with strong hydrochloric acid for about three minutes. The whole went in solution which on evaporation yielded the free basic thiodiazole. It was filtered and further purified by crystallisation from water, m.p. 232°. (Found: N, 31·57. $C_3H_5N_3OS$ requires N, 32·06 per cent.).

Hydrazo-monothio-allyl-dicarbonamide.

Semicarbazide hydrochloride (5 g.) was dissolved in water and treated with anhydrous sodium carbonate (2·4 g.) to liberate the free base. The solution was then boiled on a water-bath with an alcoholic solution of allyl mustard oil (4·5 g.) for five minutes when crystals of the hydrazide began to separate as shining plates. The reaction was complete within ten minutes. The hydrazide was purified by crystallisation from alcohol; m.p. 202°. (Found: N, 32·52. $C_5H_{10}ON_4S$ requires N, 32·18 per cent.).

2-Allylimino-3-acetyl-5-keto-2: 3: 4: 5-tetrahydro-1: 3: 4-thiodiazole.—A few grams of the hydrazide were just covered with acetic anhydride and heated under reflux over a small free flame until a clear solution was obtained. On pouring the solution into water, an oil separated which solidified on keeping under water for a few days. The yield of the solid was very small and the presence of a considerable quantity of mustard oil was detected which showed that the major portion of the hydrazide had undergone decomposition. The solid was washed with ether and crystallised from alcohol; m.p. 137°. The yield was so small that no further investigation of the substance was possible.

The experiment was repeated by heating the hydrazide with acetic anhydride on a water-bath instead of over a free flame with a view to avoid decomposition. Fortunately enough the separated oil, soon solidified yielding a much greater quantity of the substance. It was washed with ether. On attempting to crystallise the solid from

rectified spirit it was found that the solid was a mixture of two substances. The solid was dissolved by heating with 60 per cent. alcohol and filtered while hot. The filtrate yielded on cooling a crystalline substance, forming about 90 per cent. of the entire mass. It was again crystallised from rectified spirit ; m.p. 171°. (Found: N, 21·33 ; S, 15·65. The monoacetyl compound, $C_7H_9O_2N_3S$ requires N, 21·11 ; S, 16·08 per cent.).

The substance dissolves in cold dilute alkali but is not acted on by oxidising agents such as iodine solution or hydrogen peroxide. It was deacetylated by heating with moderately strong HCl when it went into solution. On concentration crystals of the free thiodiazole derivative came out; m.p. 210°. (Found: N, 26·83. $C_5H_7ON_3S$ requires N, 26·75 per cent.).

The mother-liquor was concentrated on a water-bath to a very small bulk, filtered and allowed to cool when a white crystalline substance came out; m.p. 269°. The substance was sparingly soluble in cold alkali, but more in hot, evolving the smell of *iso*cyanide all the while. The yield was only 0·05 g. and so it could not be analysed.

Hydrazo-monothio-phenyl-dicarbonamide (III) *and Acetic anhydride. Formation of* 2-*Phenyl-imino*-3-*acetyl*-5-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole and* 2-*Phenylimino*-3 : 4-*diacetyl*-5-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole*.

The hydrazide NH_2-CO-NH-NH-CS-NHPh prepared according to the method of Arndt Milde and Tschenscher (*Ber.*, 1922, **55**, 349) was heated over a small flame with so much of acetic anhydride as was just sufficient to cover it, in presence of a little well powdered fused sodium acetate. The clear solution thus obtained was poured into water when an oil giving out a strong smell of phenyl mustard oil separated which solidified on keeping under water for a few days. The yellow solid, so obtained was washed successively with rectified spirit and ether to free it from the adhering mustard oil. It was dissolved in boiling dilute alcohol, the solution was filtered and the filtrate was allowed to stand for some time while a good quantity of crystals separated. They were filtered off and the mother-liquor on concentration gave another crop of crystals of different shape and appearance from the former. The two portions were separately collected and gave different and fairly sharp melting points (210°-211°) and (171°-172°) respectively. After recrystallisation from

dilute alcohol, the first portion melted at 213° and was the diacetyl compound. (Found: N, 15·47. $C_{12}H_{11}O_3N_3S$ requires N, 15 per cent.).

The second portion melted at 173° and was the monoacetyl compound. (Found: N, 18·01. $C_{10}H_9O_2N_3S$ requires N, 17·95 per cent.).

Hydrolysis of the above Acetyl Compounds. Formation of 2-*Phenylimino-5-keto-tetrahydro*-1 : 3 : 4-*thiodiazole.*

The above acetyl compounds were separately hydrolysed with strong HCl. A crystalline white precipitate was slowly thrown out of the solution on adding water which was crystallised from dilute alcohol. The same substance was obtained from both of the acetyl compounds and melted at 206°. It slowly dissolves in cold dilute alkali with the development of a pale green colour and evolution of the disagreeable smell of *iso*cyanide. (Found: N, 21·98. $C_8H_7ON_3S$ requires N, 21·76 per cent.).

The hydrazide was also heated with acetic anhydride in presence of a small quantity of fused sodium acetate on a water-bath instead of over a free flame and the yield was thus found to be greatly increased. Only a small fraction of the hydrazide was acted on during a period of two hours. Only the monoacetyl compound was obtained in this way.

Hydrazo-monothio-ortho*tolyl-dicarbonamide* (IV).

Semicarbazide hydrochloride (5 g.) dissolved in the least quantity of water was treated with anhydrous sodium carbonate (2·4 g.) and this was heated under reflux with *o*-tolyl mustard oil (6·6 g.) for some twenty minutes while the hydrazide separated as a white solid. It was crystallised from alcohol; m.p. 201° with decomposition. (Found: N, 25·12. $C_9H_{12}ON_4S$ requires N, 25·00 per cent.).

2-*o*-*Tolylimino*-3-*acetyl*-5-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*thiodiazole.*

The above hydrazide was covered with acetic anhydride in presence of a little powdered fused sodium acetate and carefully heated with a small flame which was removed as soon as the reaction commenced which however, came to an end by itself yielding a clear solution which gave an oily product on being poured into water. After 24 hours' standing the solidified oil was washed well with

alcohol and ether to remove the adhering mustard oil, etc., and crystallised from rectified spirit ; m.p. 183°. (Found : N, 17·10. $C_{11}H_{11}O_2N_3S$ requires N, 16·87 per cent.).

2-o-Tolylimino-5-keto-tetrahydro-1 : 3 : 4-thiodiazole.

The above acetyl compound was boiled under reflux with fuming hydrochloric acid but it did not go into solution. The solid product was washed with water, dried and crystallised from a large quantity of dilute alcohol; m.p. 210°. (Found: N, 20·44. $C_9H_9ON_3S$ requires N, 20·29 per cent.).

Hydrazomonothio-p-tolyl-dicarbonamide (V).

Semicarbazide hydrochloride (5 g.) dissolved in the least quantity of water was treated with anhydrous sodium carbonate (2·4 g.) and the solution was boiled under reflux with *p*-tolyl mustard oil (6·6 g.) After 15 minutes' boiling crystals of the hydrazdie began to separate and the reaction came to an end after about half an hour. It was crystallised from alcohol; m.p. 192°. (Found : N, 25·32. $C_9H_{12}ON_4S$ requires N, 25·00 per cent.).

Hydrazo-monothio-p-tolyl-dicarbonamide and Acetic Anhydride. Formation of 2-p-Tolyl-imino-5-keto-2 : 3 : 4 : 5 tetrahydro-1 : 3 : 4 thiodiazole and p-Tolyl-2-imino-5-thiol-3-acetyl-2 : 3-dihydro-1 : 3 : 4-triazole.

The clear solution obtained within a few minutes' heating was poured into cold water and allowed to stand overnight. Next morning the oil was found to have partially solidified with a layer of crystals deposited over it. The white solid that came out of itself from the aqueous solution was carefully collected and crystallised from rectified spirit ; m.p. 247°. It was 2-*o*-tolylimino-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole. It was insoluble in alkali and remained unchanged on being boiled with fuming hydrochloric acid pointing to the fact that there was no acetyl group present in it. (Found: N, 20·61. $C_9H_9ON_3S$ requires N, 20·29 per cent.). The solidified oil was washed carefully with ether and crystallised twice from rectified spirit; m.p. 154°. It readily dissolves in alkali from which acid precipitates it. It is acted on by $FeCl_3$, H_2O_2 and iodine solution. It is 2-*o*-tolylimino-3-acetyl-5-thiol-2 : 3-dihydro-

1:3:4-triazole. (Found: N, 21·97 ; S, 12·83. $C_{11}H_{12}ON_4S$ requires N, 22·58 ; S, 12·90 per cent.).

As the quantity was very small it could not be deacetylated with hydrochloric acid.

Hydrazo-monothio-xylyl-dicarbonamide (VI).

Semicarbazide hydrochloride (5 g.) dissolved in a small quantity of water was treated with anhydrous sodium carbonate (2·4 g.) and boiled under reflux with xylyl mustard oil (7·2 g.) in presence of about 200 c.c. alcohol. Within half an hour the reaction was complete and the separated solid was crystallised from alcohol, m.p. 200° with decomposition. (Found: N, 23·81. $C_{10}H_{14}ON_4S$ requires N, 23·53 per cent.).

2-Xylylimino-3-acetyl-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole.—The hydrazide was treated as usual with fused sodium acetate and acetic anhydride and within two minutes a clear solution was obtained which was poured into water. An oil separated out smelling strongly of mustard oil and solidified after 24 hours. It was washed with ether and crystallised from rectified spirit, m.p. 218°. (Found : N, 16·00. $C_{12}H_{13}O_2N_3S$ requires N, 15·97 per cent.).

Hydrolysis of the above compound : The free Thiodiazole derivative.—The above acetyl compound was boiled for half an hour under reflux with fuming hydrochloric acid, and the product was crystallised from rectified spirit; m.p. 232°. The substance slowly dissolved in cold dilute alkali with a pinkish colour which disappears on boiling but reappears on cooling. (Found: N, 18·68. $C_{10}H_{11}ON_3S$ requires N, 19·00 per cent.).

Hydrazomonothio-β-naphthyl-dicarbonamide (VII).

β-Naphthyl mustard oil (5 g.) was dissolved in alcohol by warming (VII) and to this was added an aqueous solution of semicarbazide hydrochloride treated previously with (3 g.) anhydrous sodium carbonate (1·4 g.). The mixture was then gently boiled under reflux for about 10 minutes and the separated hydrazide after washing with alcohol was crystallised from a large volume of the same solvent ; m.p. 210° (decomp.). (Found: N, 21·10. $C_{12}H_{12}ON_4S$ requires N, 21·54 per cent.).

The hydrazide on being heated with acetic anhydride (though extremely carefully) decomposed completely. Among the decomposition products almost the calculated quantity of β-naphthyl-mustard oil was isolated and identified.

Hydrazo-monothiophenyl dicarbonamide (VIII) *and AceticAnhydride. Formation of 2-Imino-3-acetyl-5-keto-2:3:4:5-tetrahydro-1:3:4-thiodiazole and 2-Imino-3:4-diacetyl-5-keto-2:3:4:5-tetrahydro-1:3:4-thiodiazole.*

Hydrazo-monothiophenyl-dicarbonamide, Ph-NH-CO-NH-NH $CSNH_2$ prepared from phenyl *iso*cyanate and thiosemicarbazide according to Freund and Schander (*Ber.*, 1896, **29**, 2510) was treated with acetic anhydride in the usual way. The solid obtained from the oil after 24 hours was crystallised from rectified spirit, m.p. 275°. (Found: N, 26·52, 26·72; S, 19·90. The monoacetyl compound, $C_4H_5O_2N_3S$ requires N, 26·42 ; S, 20·13 per cent.).

The solution after the separation of the solidified oil was concentrated to a small bulk, and steam was passed through it until the solution was almost free of acetic acid. The volume of the solution was again considerably reduced by evaporating on a water-bath and crystals came out on cooling. It was finally crystallised from a mixture of water and alcohol, m.p. 162°. (Found: N, 21·04. The diacetyl compound, $C_9H_7O_3N_3S$ requires N, 20·90 per cent.).

The free thiodiazole derivatives could not be prepared by deacetylation with HCl for want of sufficient quantity of the acetyl derivatives.

In another experiment the hydrazide was boiled with an excess of acetic anhydride for about 10 minutes and the clear solution was found to emit the pungent smell of phenyl *iso*cyanate. The reaction mixture on being poured into water gave an oil which solidified on standing and from this diphenylurea, m.p. 236° and acetanilide, m.p. 113° were isolated. The aqueous solution was evaporated to a syrupy consistency and kept in a KOH-desiccator under vacuum for two to three days even when it was found not to solidify. It was then dissolved in water and passed through steam until free from acetic acid and evaporated almost to dryness. On cooling a solid separated which was found to be partially soluble in sodium hydroxide solution. This alkaline solution after acidification was evaporated to dryness, extracted with absolute alcohol and the alcoholic extract gave on concentration and cooling a crystalline mass, m.p. 92-93°. (Found: N, 24·7 ; S, 18·67 per cent.).

The alkali insoluble solid on repeated fractional crystallisation from spirit yielded two distinct compounds melting respectively at 115° and 296°. The former one on analysis gave C, 42·61 ; H, 5·01. The compound melting at 296° gave S, 19·2; N, 26·72 ($C_4H_5O_2N_3S$ requires S, 20·13 ; N, 26·42) and is evidently identical with acetyl iminothiobiazolone of Guha (*J. Amer. Chem. Soc.*, 1923 **55**, 1042).

Hydrazo-monothio-sym.-diphenyl-dicarbonamide (IX) *and Acetic Anhydride. Formation of 1-Phenyl-2-phenylimino-5-thiol-2:3-dihydro-1:3:4-triazole.*

Hydrazo-monothio-sym.-diphenyldicarbonamide, was prepared from 4-phenylthiosemicarbazide and phenyl *iso*cyanate. The solidified oil obtained after the usual treatment was taken on a filter, washed with ether and crystallised twice from alcohol. It melted at 208°. The substance was soluble in alkali. Nothing other than itself was obtained by boiling the substance with strong HCl showing thereby that no acetyl group was present. (Found: N, 21·06. $C_{14}H_{12}N_4S$ requires N, 20·90 per cent.).

On heating the hydrazide with excess of acetic anhydride for about ten minutes the main reaction product was found to be diphenyl urea, m.p. 236° mixed with a small quantity of the alkali soluble substance, m.p. 208°.

Hydrazomonothio-α-naphthyl dicarbonamide (X).

Thiosemicarbazide (4 g.) was dissolved in the least quantity of boiling water, and to the solution was added a few drops of acetic acid. To this solution was gradually added a solution of α-naphthyl *iso*cyanate (7·4 g.) in about 200 c.c of absolute alcohol. A vigorous reaction took place instantaneously, and the hydrazide came out as a white solid and was crystallised from rectified spirit; m.p. 213°. (Found: N, 21·68. $C_{12}H_{12}ON_4S$ requires N, 21·54 per cent.).

Hydrazo-monothio-α-naphthyl-dicarbonamide and Acetic Anhydride.

The hydrazide was covered with acetic anhydride in presence of a little powdered fused sodium acetate and gently heated to boiling for about 5 minutes and the turbid solution thus obtained was poured into water through a filter. The separated oil was stirred vigorously for ten minutes with hot water and within an hour or so the oil solidified which was freed from the

admixed tar by washing successively with acetone ether and benzene It was then crystallised twice from boiling pyridine; m.p. 293°. The compound contains no sulphur, is insoluble in acid and alkali and in all solvents excepting boiling pyridine. (Found: N, 9·18 per cent.). So it is nothing but sym.-α:α'-dinaphthyl urea (Cal. N, 8·97 per cent.).

Hydrazo-dicarbonamide (XI) *and Acetic Anhydride: Formation of Sym-diacetyl hydrazine.*

Hydrazo dicarbonamide (10 g.) prepared according to the method of Thiele (*Annalen*, 1892, **271**. 27) was heated with 30-40 c.c. of pure acetic anhydride in a sealed tube at 200° in an oil-bath for two hours when the whole of the substance went in solution Next day, the tube was opened. It opened with great violence, and the escaping gas was identified to be carbon dioxide. The solution was filtered from a small quantity of unreacted hydrazodicarbonamide and steam was passed through the solution for four hours in order to remove as much of acetic acid as possible. The solution was then evaporated to a brown syrupy consistency on the water-bath and after cooling was dissolved in acetone. The acetone solution was then boiled under reflux for thirty minutes with animal charcoal. After filtration and concentration, excess of ether was added to the cold syrupy mass under vigorous stirring when a beautiful crystalline mass separated out. It was purified by precipitating again from an acetone solution and was finally crystallised from benzene; m.p. 139° (yield, 4 gms.). It was proved to be sym.-diacetylhydrazine (m.p. 138°) and on being heated with strong HCl gave hydrazine dihydrochloride, m.p. 200°.

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On the Hemolytic Behaviour of Mixture of Hemolytes.

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In a previous paper we have studied the nature of the time-dilution curves of several hemolytic systems and it was found that the presence of sodium hydroxide has a definite effect on the activity of other hemolytic substances. Thus saponin and taurocholate hemolysis are to a great extent inhibited if a small quantity of sodium hydroxide, which is itself a hemolytic agent in greater concentrations, is present beforehand. With oleate and caustic soda mixture the relations however were not so simple. These experiments were thus really made in systems in which two hemolytic substances were present. Much investigation has however not been made in this particular side, namely, hemolysis by mixture of hemolytes. In an early paper Moore, Wilson and Hutchinson (*Biochem. J.*, 1909, **4**, 346) studied what they called the balancing action of certain pairs of hemolysers in preventing hemolysis and showed that there was an inhibiting action observed when sodium linoleate was used in conjunction with a pig serum both of which have a hemolytic action on sheep's corpuscles. They further observed that when a mixture of sodium oleate and linoleate was used no such inhibition was to be observed. A little earlier to this paper, Arrhenius (*Biochem. Zeit.*, 1908, **11**, 161) found that sodium oleate increases the action of cobra poison but diminishes that of saponin. This statement is taken from the abstracts, and is mentioned here because we have been unable to confirm the latter part of it. Besides these, though stray references can be obtained, there is not much material in the nature of a comparative study of the subject. The present investigation was carried out with the object of determining (1) if there is any antagonistic action between two hemolysers of similar nature, and (2) if there is no inhibiting action, then whether the effect is additive or a greatly accelerating one. These experiments were expected to throw some light on the nature of the action exerted by these hemolytes on the corpuscle surface. In the present work we have studied saponin, taurocholate, oleate and acid as the hymolysing substances, and have obtained results with a mixture in varying proportions of any two of some of these hemolysers.

Experimental.

The method of experimentation is the same as given in our previous paper, but an important variation in one procedure was adopted. It was stated in the previous paper that special care must be taken in the preparation of solutions of some of these hemolysers, because in the cases of saponin, taurocholate and oleate, the solutions lose much of their hemolytic powers on standing and as such had to be prepared fresh each time. This naturally introduced considerable difficulty in the rapid determination of hemolysis specially when large number of data had to be collected. In order to obviate this difficulty, it was decided to make a simultaneous determination of the time-dilution data of the pure hemolytes along with those of the mixture of the hemolytes everytime. In this way the making of fresh solutions too many times was avoided. Too old solutions however could not be used, and in practice the solutions were utilised so long as they remained clear without any turbidity. The hemolytic powers of the solutions were however affected by even one day's standing, and hence in the results given later on, some variation will be observed in the different series with the same hemolyte. Since however the results in each table are absolutely comparative, no difficulty will be experienced in the interpretation of the results. In the following experiments sheep's corpuscle has been used, the concentration being one c.c. of an one per cent. suspension. The total volume has been 5 c.c. The concentration of saponin is 1 in 1000, that of taurocholate 0·3 per cent., potassium oleate 1 in 10,000 and that of hydrochloric acid is N/100. The following tables give the results. All solutions have been made in isotonic saline.

Table I.

Hemolysis by mixture of saponin and taurocholate.

Amount of saponin in c.c.	Time in minutes of hemolysis in presence of taurocholate—c.c.			
	0	0·1	0·2	0·3
0·0	—	No hemolysis in 2 hours.	37 mins. 25 secs.	17 mins. 40 secs
0·05	No hemolysis in 3 hours.	—	—	—
0·10	80% hemolysis in 3 hours.	—	—	—
0·15	84	—	—	—
0·20	56	54	9	—
0·30	20	16 mins. 20 secs.	4 mins. 10 secs.	2 mins. 2 secs.
0·40	13½	3 ,, 15 ,,	1 ,, 15 ,,	—
0·60	4½	0 ,, 48 ,,	0 ,, 30 ,,	—
0·80	2½	0 ,, 40 ,,	0 ,, 15 ,,	—
1·00	1 min. 15 secs.	—	—	—

TABLE II.

Hemolysis by mixture of oleate and taurocholate.

Amount of oleate in c.c.	Time in minutes of hemolysis in presence of taurocholate—c.c.				
	0	0·1	0·2	0·3	0·4
0·0	—	No hemolysis in 2 hours.	56	29	14
0·2	No hemolysis in 2 hours.	85 mins. 27 secs.	22 mins. 40 secs.	10 mins. 20 secs.	6
0·3	30% hemolysis in 2 hours.	23 ,, 33 ,,	11 ,, 5 ,,	6 ,, 45 ,,	3 mins. 49 secs.
0·4	43 mins. 20 secs.	15 ,, 58 ,,	6 ,, 23 ,,	5 ,, 7 ,,	2 ,, 46 ,,
0·5	22 ,, 0 ,,	8 ,, 42 ,,	5 ,, 18 ,,	3 ,, 26 ,,	2 ,, 11 ,,
0·6	12 ,, 8 ,,	7 ,, 7 ,,	4 ,, 14 ,,	2 ,, 19 ,,	1 ,, 40 ,,

TABLE III.

Hemolysis by mixture of saponin and oleate.

Saponin in c.c.	Time in minutes for hemolysis in presence of oleate in c.c.				
	0	0·1	0·2	0·3	0·4
0·0	—	No hemolysis in 1½ hours.	No hemolysis in 1½ hours.	No hemolysis in 1½ hours.	80
0·2	48	21	10 mins. 45 secs.	3 mins. 9 secs.	1 mins. 10 secs.
0·3	19 mins. 9 secs.	8 mins. 5 secs.	2 ,, 25 ,,	2 ,, 0 ,,	0 ,, 40 ,,
0·4	11 ,, 10 ,,	4 ,, 40 ,,	1 ,, 34 ,,	1 ,, 0 ,,	0 ,, 35 ,,
0·5	6 ,, 35 ,,	2 ,, 4 ,,	1 ,, 0 ,,	0 ,, 46 ,,	—
0·6	4 ,, 2 ,,	1 ,, 32 ,,	0 ,, 50 ,,	0 ,, 27 ,,	—

TABLE IV.

Hemolysis by mixture of taurocholate and saponin.

Taurocholate in c.c.	Time of hemolysis in presence of saponin in c.c.				
	0	0·1	0·2	0·3	0·4
0·0	—	No hemolysis in 1 hour.	20 mins. 20 secs.	8 mins. 48 secs.	3 mins. 53 secs.
0·2	35 mins. 40 secs.	—	7 ,, 58 ,,	2 ,, 5 ,,	1 ,, 9 ,,
0·3	12 ,, 46 ,,	—	3 ,, 48 ,,	1 ,, 29 ,,	0 ,, 46 ,,
0·4	6 ,, 50 ,,	6 mins. 46 secs.	3 ,, 16 ,,	1 ,, 4 ,,	0 ,, 39 ,,
0·5	5 ,, 12 ,,	4 ,, 30 ,,	2 ,, 40 ,,	0 ,, 50 ,,	0 ,, 28 ,,
0·6	2 ,, 50 ,,	2 ,, 16 ,,	1 ,, 50 ,,	0 ,, 40 ,,	0 ,, 22 ,,

TABLE V.

Hemolysis by hydrochloric acid.

Amount of HCl in c.c.	Final concentration.	Time of hemolysis.
0·1	N/5000	No hemolysis within 2 hours.
0·2	N/2500	Slight hemolysis within 2 hours.
0·3	N/1666	Slight hemolysis in 2 hours.
0·4	N/1250	22 mins. 23 secs.
0·5	N/1000	6 mins. 33 secs.

TABLE VI.

Hemolysis by mixture of saponin and acid.

Saponin in c.c.	Time of hemolysis in presence of acid—c.c.		
	0	0·05	0·1
0·0	—	No hemolysis in 2 hours	No hemolysis in 2 hours
0·2	21 mins. 16 secs.	18 mins. 22 secs.	4 mins. 20 secs.
0·3	10 mins. 38 secs.	5 mins. 53 secs.	1 min. 26 secs.
0·4	6 mins. 27 secs.	2 mins. 43 secs.	0 min. 49 secs.
0·5	2 mins. 57 secs.	1 min. 17 secs.	0 min. 30 secs.
0·6	2 mins. 6 secs.	1 min. 0 sec.	0 min. 20 secs.

TABLE VII.

Hemolysis by mixture of oleate and acid.

Oleate in c.c.	Time of hemolysis in presence of HCl in c.c.	
	0	0·1
0·0	—	No hemolysis in 2 hours.
0·4	34 mins. 4 secs.	No hemolysis in 1 hour.
0·5	13 mins. 50 secs.	15 mins. 28 secs.
0·6	8 mins. 1 sec.	12 mins. 21 secs.
0·8	2 mins. 45 secs.	10 mins. 31 secs.
1·0	1 min. 40 secs.	9 mins. 42 secs.

TABLE VIII.

Hemolysis by mixture of taurocholate and acid.

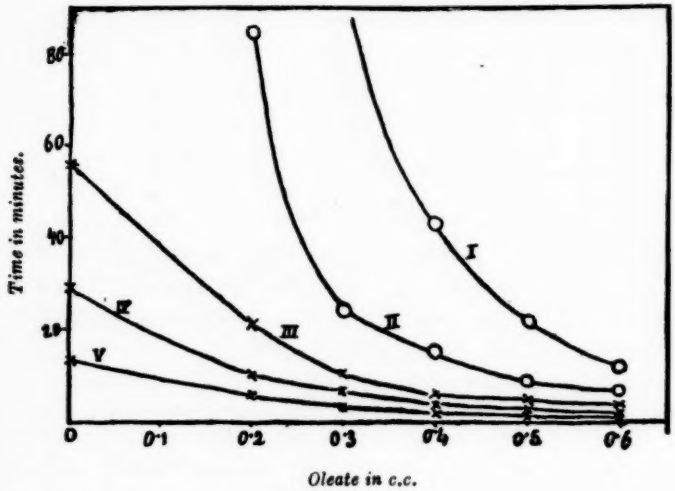
Taurocholate in c.c.	Time of hemolysis in presence of HCl in c.c.	
	0	0·1
0·0	—	No hemolysis in 2 hours.
0·4	11 mins. 32 secs.	5 mins. 33 secs.
0·5	6 mins. 8 secs.	3 mins. 40 secs.
0·6	4 mins. 0 sec.	3 mins. 1 sec.
0·7	1 min. 51 secs.	1 min. 49 secs.
0·8	1 min. 39 secs.	1 min. 39 secs.

Discussion.

The experimental results given in the previous pages all show that each hemolyte has a definite effect in presence of another hemolyte, and in the majority of cases this action is an accelerating one. It will be remembered that in our previous paper we have found that sodium hydroxide has an inhibiting effect in the case of several hemolytes. Several years ago, Ponder (*Proc. Roy. Soc.*, 1926, B, **99**, 461) studied some cases of acceleration or retardation of hemolysis and showed that in saponin hemolysis, substances like acetic acid, glutaminic acid, histidine monohydrochloride, aspartic acid and potassium chloride accelerate the hemolysis to a great extent, while sucrose, sodium hydroxide, arginine and serum inhibit the hemolysis. Aspartic acid also accelerates hemolysis by bile salts and by soaps, and is itself an hemolyser at higher concentrations. If we now look to our data given in the previous pages, it will be found that in some cases the accelerating action appears to be much greater than what we can expect if the effects are simply additive. For example, taking a particular case of oleate and taurocholate mixture (Table II) it will be seen that 0·2 c.c. of oleate or 0·1 c.c. of taurocholate does not hemolyse the corpuscles at all when used separately within two hours, but when mixed together the hemolysis is complete within 85 minutes, whereas with 0·3 c.c. oleate even, only partial hemolysis is obtained within two hours. Of course this is not absolutely inconsistent with an additive effect, and it is not possible

to state definitely in every case that this effect is more than an additive effect. It will be noticed also that contrary to the observations of Arrhenius, oleate accelerates saponin hemolysis to a great extent (Table III). In the figure the results with a single mixture of oleate and taurocholate are graphically shown. Other

Hemolytic curves of oleate in presence of varying amounts of taurocholate.



I. Pure oleate. II. Taurocholate 0·1 c.c.
III. Taurocholate 0·2 c.c. IV. Taurocholate 0·3 c.c. V. Taurocholate 0·4 c.c.

data are not plotted graphically because the nature of the curves is similar in every table. It will be noticed in these curves that with the gradual addition of the second hemolyte, the accelerating action also gradually increases. In every case the time —dilution curves with the mixture of the hemolytes are normal, and this shows that each hemolyte is also acting in a normal way in presence of another hemolyte.

The accelerating effect of acid on the action of other hemolytes deserves further consideration. Since alkali retards hemolysis while acid accelerates, the obvious conclusion would be that the hemolysis is influenced by the p_H of the solutions. That this is undoubtedly an important factor would be evident from the fact that corpuscles are hemolysed when the p_H of the solution is below 5. With alkali there is a wide zone of resistance. As a matter of fact, it was

shown in a previous paper (Sen and Basu, this *Journal*, 1928, **5**, 17) that we can expect a retarding action on hemolysis by OH' ions up to a certain concentration on theoretical grounds. The researches of Eggerth and of Mond are in this line. Eggerth (*Jour. Gen. Physiol.*, 1924, **6**, 587) found that when washed sheep's corpuscle is suspended in solutions of p_H 5·2 or more acid, it becomes progressively more electropositive, and this change is coincident with hemolysis. In investigating the hemolytic power of $H^{\cdot}$ and OH' ions Mond (*Pflug. Archiv.*, 1925, **208**, 57) found that a slight decrease in p_H from neutrality causes hemolysis, but on the alkaline side of the neutral point there is a wide zone of resistance. This can be easily exemplified in the case of saponin where we have shown that traces of acid accelerate the hemolysis, while traces of alkali retard it. With taurocholate also a similar thing happens, but a difficulty was experienced in the actual determination of the end-point in hemolysis. On standing, the hemolysed solution in presence of taurocholate and acid develops an well-marked turbidity which interfered with the accurate determination of the end-point. An identical behaviour was observed with aspartic acid by Ponder who, by the way, thought that in the acceleration or retardation of hemolysis, the nature of the accelerator or retarder has also an effect besides the change in the p_H of the solutions. It may be, that due to this appearance of turbidity, the times of hemolysis in presence or absence of acid were found to be practically the same when higher concentrations of taurocholate were used, but with lower concentrations of taurocholate a well marked acceleration was observed. In the case of oleate however, the case is just the reverse. Acids inhibit the hemolysis by oleate and it may be remembered that alkali has the opposite effect in certain concentrations of the oleate. The action of acid is undoubtedly due to a chemical interaction with the oleate liberating oleic acid which is a poor hemolytic agent. For this reason there is a great retardation of hemolysis when a mixture of oleate and acid is used. Since this chemical action must also take place when taurocholate and acid are mixed, it is to be considered that taurocholic acid is also a good hemolytic agent, and its efficiency is comparable to that of the salt at least up to certain concentrations. So far as oleate is concerned, it is certain that the salt is the active hemolyser, whilst the acid is a poor hemolytic agent. Hence the peculiar effect of alkali in accelerating the hemolytic power of oleate in low concentrations

may be due to a checking of the hydrolysis of the oleate into free acid which would otherwise take place in so dilute solutions in the absence of alkali. The effect of acids thus differ in a marked way from that of the alkali when the action of mixtures of hemolytes is considered.

Summary.

(1) An experimental investigation has been made of the hemolysis of sheep's erythrocytes by mixture of hemolytic substances.

(2) It is found that there is no balancing action when mixtures like saponin and taurocholate, saponin and oleate and oleate and taurocholate are used. It is observed that there is always an accelerating effect of one hemolyte in presence of another. The total effect of mixtures is in most cases probably additive, but in some cases there appears to be a greater than additive action.

(3) Hydrochloric acid markedly accelerates the hemolytic action of saponin. It also accelerates the action of taurocholate when the latter is in low concentrations. The hemolytic action of oleate is however considerably retarded in the presence of acid which is due to the formation of less hemolytic oleic acid.

(4) The effect of alkali is in most cases the reverse of that of acid. Saponin and taurocholate hemolysis are retarded in presence of this substance while oleate hemolysis is increased in low concentrations. This is probably due to a checking of hydrolysis of potassium oleate in dilute solutions since it has been observed that the products of hydrolysis are very weak hemolytes.

In our next paper we hope to communicate some results of a study of the balancing action of a hemolytic serum in presence of other chemical hemolysers. The oleate hemolysis in presence of alkali is also being more thoroughly investigated.

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The Inhibition of certain Photochemical Reactions by Oxygen.

By H. B. Dunnicliff and Janki Nath Joshi.

Since 1855 when Bunsen and Roscoe (Ostwald Klassiker B 34 and 38) first stated that the induction period of the reaction between hydrogen and chlorine was reduced and even eliminated by oxygen, much has been done in this field of research, the latest work showing that oxygen retards the reaction. The subject is ably summarised and detailed references are given in "A Treatise on Physical Chemistry" by H. S. Taylor (Vol. II, p. 1208, *et seq.*).

The work to be reported was undertaken to ascertain whether this behaviour of oxygen is general or is confined to the photochemical reaction between hydrogen and chlorine. The action of oxygen on several photosensitive reactions has been studied.

The photochemical reaction between mercuric chloride and ammonium oxalate (Eder's solution) was first investigated.

Winther (*Zeit. Wissen. Photo.*, 1901, 7, 409) studied the kinetics of this reaction and ascribed the precipitation of mercurous chloride and the reduction of the oxalate to the photosensitization of the non-fluorescing ferric ions which are thereby reduced to the ferrous state. This interpretation is not correct as the reaction proceeds in the absence of ferric ions according to the equation:

$$2HgCl_2 + (NH_4)_2C_2O_4 = 2HgCl + 2NH_4Cl + 2CO_2.$$

Purified mercuric chloride and ammonium oxalate were made up to 3% solutions with boiled distilled water and stored in light-proof bottles. The absence of iron was carefully proved. The progress of the reaction was measured by filtering off the mercurous chloride formed through a Gooch crucible and weighing it after drying to constant weight at 103°. The filtrate is received in a blackened conical flask to protect it from the light as, if the first filtrate is not clear the solution is again sucked through the Gooch. Winther claims that there is a limit to the amount of photochemical decomposition of Eder's solution and states that, owing to the formation of a negative catalyst, the filtrate is not photosensitive. In the course of this work it has been found that, even after ten hours'

exposure to a carbon arc, light still causes the separation of mercurous chloride from the filtered liquid.

Experiments in Vacuo.

In each of two similar rectangular bottles, 20 c.c. of each of the two solutions were taken and thoroughly mixed. One of the bottles was provided with a stop-cock and it was evacuated whilst being shaken. The two bottles were fixed at equal distances from a carbon arc and both exposed for the same intervals of time. In all cases a similar blank control containing the reaction mixture exposed to air was employed to allow for any inequalities in the burning of carbon rods.

Time (hours)	0·5	1·0	2·0	4·0	6·0	10·0	
In vacuo	12	25	40	92	148	265	mgms. of HgCl.
In air	9	16	33	66	107	174	

The amount of mercurous chloride is roughly proportional to the time of exposure. More precipitate is formed in vacuo than when some oxygen (air) is present in the solution.

Experiments with Oxygen.

The two bottles were so arranged that through one solution a current of oxygen was passed and the other was exposed to the air as before.

Time (hours)	0·5	1·0	2·0	4·0	5·0	10·0	
Oxygen bubbled	3	7	15	22	34	54	mgms. of HgCl.
In air	8	16	33	64	106	173	

These results indicate that saturation of the solution with oxygen causes still greater inhibition of the reaction.

With Hydrogen Peroxide.

Merck's hydrogen peroxide was neutralised with the calculated quantity of baryta. It was then rendered just acid by adding a small quantity more peroxide. The solution was then stirred with precipitated barium carbonate. The filtered solution was free from acid and barium. To the same reaction mixture as before, 5 c.c. of N/2 hydrogen peroxide were added and the solutions exposed to the arc.

Time (hours)	1·0	2·0	4·0	6·0	10·0	
With H_2O_2 added	1	2	3	14	17	mgms. of HgCl.
In air	16	32	65	107	174	

Thus hydrogen peroxide has a still greater retarding effect than the saturated oxygen solution.

The Effect of Ozone.

The effect of ozone which under the stimulus of light, also gives ionic oxygen was next studied. Two tubulures of a four-necked flask accommodated the terminals of the secondary of a Tesla coil. Air was drawn in through one of the other tubulures while through the other the ozonised air was sucked into a wash-bottle containing caustic potash and thence through the Eder's solution by means of an aspirator.

Time (hours)	1·0	2·0	4·0	6·0	8·0	10·0	
With ozonised air	—	5	11	17	32	38	mgms. of HgCl.
In air	16	32	65	107	128	173	

The inhibition due to ozone is greater than that due to oxygen but less than that due to hydrogen peroxide. The results of the four preceding tables are summarised for comparison in the next table.

Time (hours)	0·5	1·0	2·0	4·0	6·0	8·0	10·0	
In vacuo	12	25	40	92	148	—	265	
In air (average)	9·5	16	32·5	65	107	—	173·5	mgms. of HgCl ppted.
Oxygen saturated	3	7	15	22	34	—	54	
Hydrogen peroxide added traces	—	1	2	3	14	—	17	
Oxygen and ozone saturated	—	—	5	11	17	32	38	

The Photo-chemical Action of Bromine on Lactic Acid in Aqueous Solution.—The subject was selected as a suitable one in the field of organic chemistry.

$$CH_3CH.(OH)COOH + Br_2 = CH_3.CO.COOH + 2HBr$$

The apparatus consisted of a glass pipette having a tap at each end and a paper scale pasted on the front surface. A 250 c.p. Mazda

lamp was set at the focus of a convex lens placed between the reaction apparatus and the lamp and gave parallel rays of uniform intensity. Pure lactic acid was dissolved in air-free water and made up to a known strength. Two grams of bromine were mixed with 500 c.c. of distilled, air-free water and the strength of the solution was accurately determined.

Bhatnagar, Gupta and Mathur (*Indian Jour. Phys.*, 1928, **2**, 243) and Ghosh and Mukherjee (*J. Indian Chem. Soc.*, 1925, **2**, 165) did not allow for loss of bromine from the solution when drawn off in a pipette. The apparatus described can be used without loss of bromine from the solution greater than that required for the atmosphere above the solution when, on withdrawing a sample, the space above the liquid increases. Equal volumes of the bromine and lactic acid solutions were used as the reaction mixture. The pipette was filled by first exhausting it and then placing one tap in the reaction mixture. On opening the cock, sufficient liquid was allowed to enter to half fill the pipette. The apparatus was placed in position in front of the lens and the upper cock was connected with a carbon dioxide apparatus. Before the first exposure, unit volume (about 20 c.c) of the mixture was run directly into excess of potassium iodide solution, carbon dioxide being allowed to enter the apparatus at the same time. The iodine so formed was titrated against N/500 sodium thiosulphate. The experiment was repeated in the presence of oxygen which was allowed to enter the apparatus as the liquid was withdrawn.

Time (minutes)	5	10	15	20	25	30	35	C.c. of $Na_2S_2O_3$ equivalent to the amt. of oxidation of lactic acid in unit volume of solution.
Oxygen present average value.	1·20	1·60	1·85	3·10	7·10	9·10	11·60	
Oxygen absent average value.	1·70	2·55	3·20	3·45	3·60	3·60	—	

The early values indicate inhibition of the action by oxygen followed by increased rate of oxidation due possibly to the formation of some catalyst which accelerates the reaction. Photo-chemical decomposition of ferric oxalate to ferrous oxalate takes place in aqueous solution according to the equation,

$$Fe_2(C_2O_4)_3 = 2FeC_2O_4 + 2CO_2.$$

Ferric oxalate solution (20 c.c.) was exposed in a rectangular cell to the light from a 1000 c.p. lamp. The cell was protected from heat

radiations by means of a slowly rotating thin glass disc, the lower half of which dipped in water. In one set of experiments the cell was covered by a glass plate and in the other, oxygen was bubbled through the solution. At intervals of one hour, 5 c.c. of the solution were withdrawn and the undecomposed ferric oxalate determined by titanous chloride (Hindrichsen, *Ber.*, 1903, **36**, 1549). Up to 8 hours the change was too small to form any definite conclusions. The work was repeated in direct sunlight and 5 c.c. of solution withdrawn at ten minute intervals. All titrations were carried out in an atmosphere of carbon dioxide.

Time (minutes).	10	20	30	40	50	60		Amount of change in terms of TiCl, equivalent to the ferric oxalate decomposed.
In air.	3·55	5·45	7·15	8·35	9·30	10·85	c.c.	
Oxygen bubbled	2·25	4·70	6·05	6·40	6·75	6·90	,,	

These figures show that oxygen inhibits this reaction also.

The Action of Light on Hydrogen Peroxide Solution.

Hydrogen peroxide (1·380 gms. per litre) which had been made just alkaline with caustic potash was tried under various circumstances. The caustic potash increases the velocity of decomposition. After each exposure, the liquid was run into excess of sulphuric acid. This stopped the reaction, neutralised the caustic potash and provided the acid necessary for the subsequent permanganate titration by which the amount of decomposition was measured. Experiments were tried using a 250 c.p. lamp and exposures up to ten hours. There was no appreciable action of oxygen, ozonised air, ordinary air or evacuation of the flask in which the reaction was proceeding.

The Effect of Light on Silver Halides in the Presence of Oxygen.

Lyman has shown that oxygen absorbs ultra-violet radiations which are the most chemically active in decomposing silver halides. An attempt was made to find out if the presence of oxygen retarded the blackening of photographic printing out paper by light. Four small similar rectangular cells were mounted on a frame in a straight line. Experiments made on pieces of paper cut from the same sheet and placed in the cells and exposed to diffused light while a different gas was passed through each cell led to anomalous results. The paper was then fastened to microscope slides by rubber bands and

placed in three cells, *a*, *b* and *c* which were filled with water and through which was bubbled (*a*) oxygen, (*b*) air and (*c*) hydrogen. The maximum shade when all had been exposed for the same time to the same diffused light was shown by the paper in cell (*c*) through which hydrogen had been passed. The darkening in cell (*a*) was a minimum. Bubbling oxygen through ferrous-sulphate-permangate titration in bright sunlight gave negative results.

The experimental work has shown that, in addition to the retarding effect of oxygen on the combination of hydrogen with chlorine under the influence of light, the following photo-sensitive reactions are inhibited by oxygen or ozone or hydrogen peroxide:—

(1) The action of ammonium oxalate on mercuric chloride.
(2) The oxidation of lactic acid by bromine water.
(3) The reduction of ferric oxalate to ferrous oxalate.
(4) The decomposition of certain silver salts.

Chapman, MacMahon and others ("Physical Chemistry," *loc. cit.*) noticed that oxygen, ozone, nitric oxide, nitrogen dioxide, chlorine peroxide, etc., have an inhibiting effect on the photo-combination of hydrogen with chlorine. The interpretation of this reaction is of fundamental importance. All the gases named are rich in oxygen and, under the influence of light or chemical action, they are capable of giving free oxygen which appears to be responsible for the inhibitory effect. "Sir J. J. Thomson observed that oxygen is one of the rare molecules as distinct from atoms which can occur with a negative charge in a positive-ray bulb.* In the photo-combination of hydrogen with chlorine when the chlorine molecule is excited by the action of light, one of its electrons is knocked out into a higher orbit and that electron is accepted by the oxygen molecule which thus acquires a negative polarity. In this way an excited molecule of chlorine is lost for the production of hydrochloric acid with the result that the speed of the reaction is retarded." Ghosh and Basu (*J. Indian Chem. Soc.*, 1928, **5**, 361) have shown that in the action of bromine on tartaric acid, several side-reactions take place, *e.g.*, in the presence of water and oxygen, hydrobromic and hypobromous acids are produced. The formation of hypobromous acid involves the loss of an

* This view is identical with the observation of J. C. Ghosh, (*Cf.* Presidential Address, Chemistry Section, Indian Science Congress, 1925).

activated molecule of bromine which reacts with oxygen and water to produce the two acids. In the case of lactic acid reported above, the mechanism appears to be identical and the loss of an activated bromine atom which reacts with oxygen in the presence of water is responsible for the decrease in the rate of the reaction.

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Sensitization of Sols of Mastic, Gum Dammar and Odèn Sulphur in Presence of Gelatine and some Carbohydrates.

By L. S. Bhatia, S. Ghosh and N. R. Dhar.

In a previous communication (Ghosh and Dhar, *Koll. Zeit.*, 1927, **41**, 229) we have explained the phenomenon of sensitization observed with some sols in presence of small amounts of hydrophilic colloids from the following points of view :—

(*i*) The hydrolysis of sols of arsenious sulphide, mastic, gamboge etc. is checked by H° ions present in sensitizers like gelatine, tannic acid, etc., which are negatively charged (compare Ghosh and Dhar, *J. Phys. Chem.*, 1925, **29**, 659 ; 1926, **30**, 830 ; *Koll. Zeit.*, 1926, **39**, 346).

(*ii*) The hydrogen ions present in some negatively charged sols cause the reversal of the negative charge on gelatine, albumin, etc.

(*iii*) Negatively charged gelatine, albumin, tannic acid, etc. can neutralise the charge on positively charged sols and thus cause precipitation of these sols.

In this paper we have investigated the influence of hydrogen ion concentration on the sensitization of the sols of mastic, gum dammar and sulphur (Odèn) in presence of small amounts of gelatine and carbohydrates. Hydrogen ion concentration of the solutions has been determined by using a vernier potentiometer (Scientific Instrument Co., Cambridge) and Hilder-brand electrode.

Mastic.

The sol was prepared by running 50 c. c. of alcoholic solution of mastic in a litre of water drop by drop from a burette at the rate of one drop per 30 seconds. Half of the sol was dialysed for a week till free from alcohol and the other half was not dialysed. The following results were obtained with the dialysed and undialysed sols.

Undialysed sol.

Concentration of the sol = 2·48 gms. of mastic per litre.
5 C. c. sol made up to 10 c. c. Time for coagulation = ½ hour.

TABLE I.

Sensitization with gelatine.

Amount of 0·5 % gelatine added in c. c.	Amount of N-KCl required to coagulate in c. c.	p_H value* of gelatine and water.	p_H value* of the mixture of mastic sol and gelatine.
0	0·9	—	4·3106 (pure sol)
0·04	0·7	6·9612	4·8062
0·08	0·45	6·9123	5·3710
0·10	0·15	6·8905	5·8162
0·20	0·25	6·7771	5·3731
0·30	0·45	6·6384	5·0109
0·40	0·55	8·5186	4·7470
0·50	0·70	6·4354	4·4696
1·00	0·80	6·3508	4·3173
1·50	1·20	6·2696	4·1904
2·00	1·60	6·1980	3·8589

TABLE II.

Sensitization with milk sugar.

Amount of 10 % milk sugar added in c. c.	Amount of N-KCl to coagulate in c. c.	p_H value of the mixture of mastic sol and milk sugar.
0	0·90	4·3106 (pure sol)
1·0	0·80	4·3359
2·0	0·70	4·4982
3·0	0·55	4·7461
4·0	1·00	4·2902

* In all cases p_H values were determined for the same concentration of gelatine as used in coagulation experiments in presence of water or the sol.

TABLE III.

Sensitisation with starch.

Amount of 2 % starch added in c. c.	Amount of N-KCl to coagulate in c. c.	pH value of the mixture of mastic sol and starch.
0	0·90	4·2971 (pure sol)†
0·5	0·80	4·3274
1·0	0·75	4·4196
1·5	0·65	4·5277
1·75	0·60	4·6572
2·0	1·00	4·2818

The starch used in these experiments was pure Merck's soluble sample and was dialysed for purification.

Dialysed sol of mastic.

Concentration of the sol = 2·46 gms. of mastic per litre.
5 C. c. of the sol made up to 10 c. c. Time for coagulation = $\frac{1}{2}$ hr.

TABLE IV.

Sensitization with gelatine.

Amount of 0·5 % gelatine added in c. c.	Amount of 2N-KCl to coagulate in c. c.	pH value of gelatine and water.	pH value of the mixture of mastic sol and gelatine.
0	2·00	—	5·5472 (pure sol)
0·04	1·70	6·9612	5·7942
0·08	1·30	6·9123	6·1478
0·10	1·00	6·8905	6·5031
0·30	1·50	6·6384	6·0615
0·50	2·20	6·4354	5·6809

† The sol becomes slightly more acid on keeping because of increased hydrolysis of the sol.

TABLE V.

Sensitization with milk sugar.

Amount of 20 % milk sugar added in c. c.	Amount of 2N-KCl to coagulate in c. c.	pH value of the mixture of mastic sol and milk sugar.
0	2·00	5·5388 (pure sol)
0·5	1·80	5·6640
1·00	1·60	5·7467
1·25	1·50	5·8535
1·50	2·20	5·5322

TABLE VI.

Sensitization with starch.

Amount of 2 % starch added in c. c.	Amount of 2N-KCl to coagulate in c. c.	pH value of the mixture of starch and the sol.
0	2·00	5·5354
0·05	1·90	5·6335
1·00	1·70	5·7148
1·25	1·60	5·8027
2·00	2·30	5·5487

The dialysed sol was exposed to sunlight for five hours and the following results were obtained with gelatine and this exposed sol.

TABLE VII.

Amount of 0·5 % gelatine added in c. c.	Amount of 2N-KCl to coagulate in c. c.	pH value of gelatine and water.	pH value of gelatine and the exposed sol.
0	1·60	——	5·0109
0·04	0·90	6·9612	5·5092
0·08	0·70	6·9123	5·8760
0·10	0·45	6·8905	6·0620
0·30	1·00	6·6384	5·6065
0·50	1·50	6·4354	5·0820

Gum dammar.

The sol of this resin is prepared in the same way as described in the case of mastic. Experiments were made with both dialysed and undialysed sols.

Undialysed sol of gum dammar.

Concentration of the sol = 2·08 gms. of gum dammar per litre.
5 C. c. of the sol made up to 10 c. c. Time for coagulation = ½ hr.

TABLE VIII.

Sensitization with gelatine.

Amount of 0·05 % gelatine added in c. c.	Amount of 2N-KCl to coagulate in c. c.	p_H value of the mixture of the sol and gelatine.
0	0·90	6·1478
0·04	0·40	6·3509
0·08	0·20	6·5561
0·10	0·35	6·8390
0·30	0·60	6·5180
0·50	1·50	6·0106

TABLE IX.

Amount of 10 % milk sugar added in c. c.	Amount of 2N-KCl to coagulate in c. c.	p_H value of the mixture of the sol and sugar.
0	0·90	6·1472
1·00	0·80	6·2459
1·50	0·70	6·3508
2·00	0·65	6·3863
2·50	1·05	6·1309

TABLE X.

Amount of 1 % starch solution added in c. c.	Amount of 2N-KCl to coagulate in c. c.	pH value of the mixture of the sol and starch.
0	0·90	6·1410
0·50	0·80	6·1918
1·00	0·75	6·2561
1·25	0·70	6·3339
1·50	0·65	6·3610
2·00	1·30	6·2275

Dialysed Sol of Gum Dammar.

Concentration of the sol = 2·01 gms. of gum dammar per litre.
5 C.c. of the sol made up to 10 c.c. Time for coagulation = $\frac{1}{2}$ hr.

TABLE XI.

Sensitization with gelatine.

Amount of 0·05 % gelatine added in c.c.	Amount of 2N-KCl to coagulate in c.c.	pH value of the mixture of the sol and gelatine.
0	1·90	6·5149
0·04	1·00	6·6367
0·08	0·80	6·7675
0·10	0·60	6·8998
0·30	1·25	6·8245
0·50	2·00	6·5065

TABLE XII.

Sensitization with milk sugar.

Amount of 10% milk sugar added in c.c.	Amount of 2N-KCl to coagulate in c.c.	pH value of the mixture of the sol and sugar.
0	1·90	6 5149
0·50	1·80	6·6147
1·00	1·70	6·7213
1·50	1·50	6·8304
2·00	2·50	6·4997

TABLE XIII.

Amount of 1% starch solution added in c.c.	Amount of 2N-KCl to coagulate in c.c.	pH value of the mixture of the sol and starch.
0	1·90	6·5149
0·50	1·80	6·5877
1·00	1·65	6·6875
1·50	2·00	6·5117
2·00	2·40	6·5018

The dialysed sol of gum dammar was exposed to sunlight for five hours and the following results were obtained with this exposed sol and gelatine.

TABLE XIV.

Amount of 0·5% gelatine added in c.c.	Amount of 2N-KCl to coagulate in c.c.	pH value of the mixture of gelatine and the sol.
0	1·30	6·2730
0·04	0·90	6·4997
0·08	0·65	6·6841
0·10	0·45	6·8465
0·30	0·85	6·5600
0·50	1·50	6·2629

Sulphur (Odén) Sol.

This sol is prepared by adding concentrated sulphuric acid drop by drop to an equal volume of 3N-sodium thiosulphate at a temperature of 20°. The mixture is now left for dialysis in a parchment bag for about 10 days.

Concentration of the sol = 2·98 grms. of sulphur per litre.

5 C.c. of the sol made up to 10 c.c. Time for coagulation = ½ hr.

TABLE XV.

Sensitisation with gelatine.

Amount of 0·5% gelatine added in c.c.	Amount of N-KCl to coagulate in c.c.	pH value of a mixture of the sol and gelatine.
0	0·60	3·3953
0·10	0·45	4·5389
0·15	0·30	5·3256
0·20	0·40	5·1734
0·40	0·45	5·1005
0·60	0·55	4·8483
0·80	0·70	4·6591

The following results were obtained when sulphur sol was sensitized by gelatine in presence of HCl.

TABLE XVI.

0·5 c.c. N/100 HCl is mixed with 5 c.c. of sulphur sol.

Amount of 0·5% gelatine added in c.c.	Amount of N-KCl to coagulate in c.c.	pH value of the mixture of the acidic sol and gelatine.
0	0·85	3·0857
0·10	0·50	4·6997
0·15	0·40	5·3390
0·20	0·45	5·1141
0·40	0·55	4·9636
0·80	0·65	4·6591

The following results were obtained when sulphur sol was sensitized by gelatine in presence of NaOH.

TABLE XVII.

0·5 c.c. N/100 NaOH is mixed with 5 c.c. sulphur sol.

Amount of 0·5% gelatine added in c.c.	Amount of N-KCl to coagulate in c.c.	p_H value of the mixture of gelatine and sol to which alkali was added.
0	0·50	3·7438
0·10	0·45	4·3139
0·15	0·35	4·9531
0·20	0·45	4·6557
0·40	>0·60	4·3309

From Tables XV, XVI and XVII it will be seen that the degree of sensitization with gelatine is greatest with the sol containing acid and it is least with the sol containing alkali.

Following results were obtained with Odèn sulphur sol and tannic acid.

TABLE XVIII.

Amount of 1% tannic acid added in c.c.	Amount of N-KCl to coagulate in c.c.	p_H value of the mixture of the sol and tannic acid.
0	0·60	3·3953
0·5	0·80	3·3057
1·0	1·00	3·2244
1·5	1·25	3·1466

From our experimental results we find that gelatine can sensitize the sols of mastic, gum dammar and Odèn sulphur when added in very small amounts. With increasing amounts of gelatine the sensitization first increases, passes through a maximum and then decreases till the sols are highly stabilised on the addition of gelatine. Sols of mastic, gum dammar and sulphur (Odèn) are more acidic than isoelectric gelatine and as gelatine is gradually added to these sols the p_H value increases and passes through a maximum and then decreases. It may be of interest to note from the experimental results that the amount of gelatine causing the maximum

p_H value also produces the maximum sensitization. These results can be explained as follows:—

When a very small amount of gelatine is added to the sol of mastic, gum dammar or sulphur (Odèn), the H° ions available from the sols are adsorbed by the negatively charged gelatine which becomes positively charged, and neutralises a part of the negative charge on the sols and thus produces a sensitization. With increasing amounts of gelatine more and more of H° ions are adsorbed from the sols by gelatine, which now produces greater number of positively charged protein micelles and develops greater degree of sensitization. When, further quantities of negatively charged gelatine are added to the sols, the hydrogen ions present in the sols are not sufficient to convert the gelatine into a positively charged colloid. Hence larger amounts of gelatine lead to the stabilisation of the sols of mastic, gum dammar and Odèn sulphur, the gelatine acting as a protecting agent.

It is obvious that maximum sensitization with a negatively charged sol should be observed only when the maximum amount of positively charged gelatine is produced. It is also apparent that when maximum amounts of positively charged gelatine are produced, the adsorption of H° ions originally present in the sol is very high and this high adsorption results in a maximum decrease in the hydrogen ion concentration in the sol and maximum increase in the p_H values. When larger amounts of gelatine are added the hydrogen ion concentration in the system increases, because gelatine itself is slightly acidic. Hence maximum sensitization coincides with the maximum p_H value of the system when the amount of gelatine added is gradually increased.

It will be seen from our results that undialysed sols of mastic and gum dammar are more sensitized than the dialysed sols. This is because the dialysed sols are less acidic than the undialysed ones. We have also found that a sol of mastic, or gum dammar becomes more acidic when exposed to sunlight due to its increased hydrolysis and hence develops greater degree of sensitization (compare Tables IV, VII, XI and XIV).

In order to show that the change in the p_H values of mastic and gum dammar is only due to gelatine, we have measured the p_H values of the sols by the addition of KCl but the p_H values of the sols did not change by the addition of KCl.

Coagulation of sulphur (Odèn) sol in presence of small amounts of acid and alkali shows that the sol becomes slightly stable in presence of an acid and unstable in presence of an alkali. In a previous publication we have shown that this behaviour is due to the fact that acids stabilise and alkalis decompose pentathionic acid which is stabilising electrolyte. Sensitization of slightly acidic or alkaline sulphur sol with gelatine has also been studied. It has been found that the degree of sensitization is developed most with acidified sol and less with the sol in which very small amounts of alkali are added. The acidified sol gives greatest amount of positively charged gelatine and hence develops maximum amount of sensitization.

In a previous paper (*Koll. Zeit.*, 1928, **44**, 218) we explained that the sensitization of mastic sol in presence of carbohydrates such as dextrin, starch and glucose observed by Boutaric (*Jour. Chem. Phys.*, 1926, **23**, 851) results from the supression of hydrolysis of the mastic sol due to the addition of carbohydrates. We have shown that mastic, which is a glucoside, hydrolyses, thus:

$$AB + H_2O \rightleftarrows AOH + HB$$

(where AOH is a carbohydrate and HB is complex acid) yielding an anion which stabilises the sol. Addition of carbohydrates decreases the hydrolysis of the sol and hence the decrease in the amount of the acid causes a decrease in the stability of the sol. Our experimental results recorded in this paper prove that the p_H value of the sol continuously increases on the addition of cane sugar or starch producing a sensitization of the sol towards electrolytes. When greater amounts of carbohydrates are added, a stabilising influence is observed and along with this we find that the p_H value of the mixture also gradually decreases. It is probable that larger amounts of sugar or starch cause a peptisation and consequent greater disintegration of colloid particles and thus produce more surface and greater hydrolysis of the colloid. Tartar and Draves (*Jour. Phys. Chem.*, 1926, **30**, 763) observed that a sol of mastic consisting of smaller particles is more acidic then a sol of bigger particles.

We have also investigated the influence of carbohydrates on the coagulation of sulphur (Odèn) sol and found that they have neither sensitizing nor protective influence. The p_H value of the sols

is also not changed by the addition of the carbohydrates to the sol.

In a recent paper William and Sugden (*J. Chem. Soc.*, 1926, **129**, 2424) have studied the sensitization of the sols of arsenious sulphide and aluminium hydroxide in presence of gelatine. They find that small amounts of gelatine sensitizes both the positively and negatively charged sols and greater amounts of gelatine stabilize them. The amounts of gelatine required to stabilize the sol increase with the increasing amounts of the coagulating electrolyte, and after a particular concentration of the electrolyte, the amount of gelatine required for stabilization instead of increasing decreases with the increase in the amounts of coagulating electrolyte. William and Sugden, therefore, conclude that the phenomenon of sensitization does not depend on charge neutralisation of sols but on some other factors.

Exactly similar results were obtained by Freundlich and Brossa (*Z. physikal. Chem.*, 1915, **89**, 306) with ferric hydroxide sol when large amounts of albumin were added to the sol. Thus a mixture of 50 c.c. albumin sol and 4 c.c. of ferric hydroxide could be completely coagulated with 6·25 millimoles of NaCl per litre but when 200 millimoles of NaCl per litre were added, the sol did not even become turbid. We are, however, of opinion that the results of William and Sugden, and Freundlich and Brossa originate from the fact that proteins are peptised by certain electrolytes. Loeb ("Proteins and the Theory of Colloidal Behaviour," 1922) has shown that the solubility of gelatine is remarkably increased in presence of certain electrolytes. Similar behaviour was also observed by Miss Chiek (*Biochem. Zeit.*, 1913, **7**, 318) with globulin suspensions.

In presence of larger quantities of electrolytes therefore proteins cannot be easily precipitated and consequently the sols are not coagulated in presence of gelatine or albumin when larger amounts of electrolytes are used though smaller quantities of electrolytes can coagulate the sols.

Freundlich ("Colloidal Behaviour" by Bogue, 1924, Vol. I, p. 297) believes that sensitization of sols of ferric hydroxide and silver (Carey Lea) is due to the neutralisation of the change on the colloid particles by the positive or negative micelles which are supposed to be simultaneously present in the same albumin solution because of the amphoteric nature of the protein. But he considers this explanation of the phenomenon of sensitization is not true in all cases and depends upon the polar structure of the amino acids.

It may be of interest to note that Kermack and Wright (*Biochem. J.*, 1923, **17**, 635) studied the precipitation of gum benzoin sol over a wide range of p_H values and found that precipitation occurred only on the acidic side of the isoelectric gelatine and protection on the alkaline side. Rideal (*Proc. Chem. Phil. Soc.*, 1924, **22**, 101) found that a gold sol can only be sensitized by gelatine when p_H value is greater than S. Kermack and MackCullum (*Proc. Roy. Soc. Edin.* 1925, **45**, 71) investigated the sensitization of cholesterol sols by gelatine over a wide range of p_H values and found that coagulation could not be observed between p_H 4·8 and 13. Coagulation, however, occurred when the alkalinity of the solution was extremely high and the precipitating effect of the cation present became prominent. Kreb (*Biochem. Zeit.*, 1928, **159**, 311), observed that the precipitation of colloidal gold occurs in presence of gelatine only when the acidity of the sol is greater than that of isoelectric gelatine. Andrejew (*Biochem. Zeit*, 1927, **65**, 182) recently concludes that only acidified solutions of protein can sensitize negatively charged sols.

We are therefore, of the opinion that the phenomenon of sensitization as observed with proteins and few negatively charged sols is a result of only neutralisation of the negatively charged on the colloid particles by positively charged proteins formed by the adsorption of some hydrogen ions present in the sol.

The sensitization observed with monovalent coagulating ions is, as a general rule, found to be more developed than in the cases of polyvalent coagulating ions. In a previous communication *J. Indian Chem. Soc.*, 1928, **5**, 303) we have shown that as the charge on a colloid is decreased, the amount of monovalent coagulating ions necessary for precipitation is decreased to a greater extent than ions of higher valencies. It is obvious that the phenomenon of sensitisation is due more to the diminution of the electric charge of the colloid particles than their dehydration.

Kruyt (*Koll. Zeit.*, 1922, **31**, 338) advances the view that the phenomenon of sensitization in the case of some negatively charged sols due to the presence of tannin originates from the dehydration of polar tannin. We have investigated the influence of tannic acid on the coagulation of sulphur (Odèn) which has been designated by Fruendlich as a lyophile colloid and found that tannic acid instead of sensitizing, protects Odèn sulphur sol. Moreover, in previous publications (*Koll. Zeit.*, 1928, **44**, 149 ; *J. Indian Chem. Soc.*, 1928, **5**, 303 we have emphasised that hydration of a colloid need not effect its stability at all.

Summary.

(1) Dialysed and undialysed sols of mastic and gum dammar and a sol of sulphur (Odèn) are sensitized towards their coagulation by KCl in presence of small amounts of gelatine. When larger amounts of gelatine are added the sols are stabilised.

(2) It is found that mastic, gum dammar and sulphur sols are acidic. When increasing amounts of gelatine are added to the sols their p_H values increase to a maximum and then decrease.

(3) The amount of gelatine producing maximum sensitization also develops maximum p_H value.

(4) Undialysed sols of mastic and gum dammar are more sensitized by gelatine than the dialysed sols. Sols exposed to sunlight are also more sensitized by gelatine than the sols kept in diffused light. It is found that both exposed and undialysed sols are more acidic than the dialysed sols.

(5) Sulphur (Odèn) sol is sensitized to a greater extent by gelatine in presence of an acid and to a smaller degree in presence of an alkali.

(6) We are of the opinion that the phenomenon of sensitization as observed with proteins and some negatively charged sols is due to charge neutralisation of the negatively charged colloid particles by positively charged proteins formed by the adsorption of some hydrogen ions present in the sols.

(7) Carbohydrates in smaller amounts have been found to sensitize mastic and gum dammar sols and increase their p_H values. This is because the carbohydrates depress the hydrolysis of mastic and gum dammar and thus decrease the amount of the complex organic acid, which stabilises the sol.

(8) Larger amounts of carbohydrates stabilise the sols of mastic and gum dammar and decrease their p_H values because of the increase in the disintegration of the colloid particles of mastic and gum dammar.

(9) Odèn sulphur sol is neither sensitized nor protected by carbohydrates. Tannic acid stabilises this sol.

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Kinetics, Quantum Efficiency and Temperature Coefficients of the Decomposition of Ferric Thiocyanate and the Bleaching of Neocyanin and some other Photochemical Reactions in Radiations of Different Frequencies.

By A. K. Bhattacharyya and N. R. Dhar.

In previous publications (*J. Chem. Soc.*, 1923, **123**, 1856; *Zeit. anorg. Chem.*, 1922, **121**, 156 ; 1928, **169**, 381) the kinetics, temperature coefficients and the quantum efficiency of several photochemical reactions have been determined in radiations of different wave-lengths.

From the results on the quantum efficiency measurements of several photochemical reactions we have deduced the conclusion that the Einstein law of photochemical equivalence generally fails in exothermal photochemical changes. Moreover, we have shown that the quantum efficiency increases with the concentration and the temperature of the reacting system.

In this communication we are submitting the results obtained in the determination of the order, temperature coefficient and the quantum efficiency of the following reactions in light of different wave-lengths: – (1) Decomposition of ferric thiocyanate; (2) bleaching of neocyanin by air ; reactions between (3) sodium lactate and iodine, (4) sodium tartrate and iodine, (5) chromic acid and citric acid, (6) chromic acid and tartaric acid and (7) chromic acid and lactic acid.

The kinetics of all the seven reactions have been determined in the dark and in the light and the quantum efficiency has been measured in radiations of different wave-lengths. The source of light was a 1000 watts gas filled tungsten filament lamp operated at 4·6 amperes. The lamp was placed in a box and an electric radiator was worked at the back of the lamp in order to keep it cool. Two big glass lenses were placed between the light source and the reaction vessel to get parallel light. To isolate different regions, a set of gelatine film filters was used. The radiomicrometer was placed at a

distance of one metre from the light source. Water at a constant temperature from a thermostat was circulated round the reaction vessel, which is a silica cube.

The changes in the reactions studied were determined either by suitable titrations or spectrophotometric measurements.

In order to determine the absorption by the reacting system in the different part of the visible spectrum the extinction coefficient has been measured by a Nutting spectrophotometer.

1. *Decomposition of ferric thiocyanate.*

Philip and Bramley (*J. Chem. Soc.*, 1913, **103**, 795) represented the decomposition of this compound in the diffused light of the laboratory by the equation:—$8Fe(CNS)_3 + 6H_2O = 8Fe(CNS)_2 + 7HCNS + CO_2 + H_2SO_4 + NH_3$.

We have observed that the decomposition is highly photosensitive and that the velocity of the reaction in the dark is negligibly small. The concentrations could be accurately determined by spectrophotometric measurements. The following results were obtained:—

Ferric chloride (N/250) *and Ammonium Sulphocyanide* (N/50) 10 c. c. *each.*

Dark:—No appreciable reaction.

Region in A°. U.	Temperature °C	k_1 Monomolecular	Temperature Coefficient.	Quantum efficiency.
(5000-4450A°)	20°	0·000509	2·12	6·3
Meanλ	30°	0·00107	...	9·2
=4725A°	40°	0·00215	2	12·4
			...	
(5850-5450A°)	20°	0·000392		5·6
			2·3	
Meanλ	30°	0·000902	...	7·3
=5650A°	40°	0·00197	2·2	11·1
(7608-7000A°)	20°	0·000284	2·5	3·4
Meanλ	30°	0·000709		4·6
=7301A°	40°	0·00163	2·3	7·3

Absorption :—

$$\text{Extinctinction coefficient} = \frac{\text{Density reading on the scale.}}{\text{Thickness of the cell.}}$$

Region in A°U.	7000	6707	5970	5670	5490	5320	5200
Extinction coefficient.	·05	·09	·10	·42	·73	1·46	2·07
Region in A°U.	5000	4910	4800	4720	4670	4550	4400
Extinction coefficient.	3·8	Beyond∞	Complete		absorption.		

2. *Bleaching of Neocyanin.*

The kinetics, energetics and temperature coefficients of bleaching of dicyanin in light have been investigated in these laboratories. We have now determined the same with neocyanin. Dilute solutions of neocyanin (Kodak) through which air was passed were exposed to light. The concentrations of the solutions were measured by the spectrophotometric method. The results are summarised in the following table :—

Neocyanin (M/7176).

Dark : —Reaction is negligible.

Region in A°U	Temperature °C	k_1 Monomolecular	Temperature coefficient.	Quantum efficiency.
(5000-4450 A°)	20°	0·000641	1·29	2·5
Mean λ	30°	0·000830	1·2	3·6
=4725	40°	0·000990	1·2	4·7
(5850 5450)	20°	0·000830	1·2	1·8
Mean λ	30°	0·000990	...	2·7
=5650	40°	0·00110	1·11	3·9
(7608-7000)	20°	0·00102	...	1·1
Mean λ	30°	0·00114	1·12	2·1
=7304	40°	0·00120	1·05	3·1

Absorption :—M/7176—*Neocyanin.*

Region in A°U.	7000	6707	5970	5670	5490	5320	5200
Extinction coefficient.	Complete absorption.		eyond∞	1·96	·86	·44	·21
Region in A°U.	5000	4910	4800	4720	4670	4550	4400
Extinction Coefficient.	·24	·27	·31	·43	·48	·54	·62

8. *Sodium lactate and iodine.*

One of us (*Proc. Akad. Wetensch. Amsterdam*, 1916, **24**, 974) observed that this reaction is photosensitive. We have now determined the kinetics, temperature co-efficients and energetics of this reaction in the dark and in radiations of different wave-lengths. The rate of the reaction was followed by estimating the unchanged iodine by thiosulphate.

The experimental results are as follows:—

Sodium lactate N/4·69 *and Iodine* N/100 *in* N/34·3-KI, 10 *c.c. each.*

Dark.	Temperature	k_1 Monomolecular	Temperature co-efficient.	Total order.
N/4·69 Lactate	20°	0·000720	—	Bimolecular
	30°	0·00179	2·49	
	40°	0·00414	2·31	
	20°	0·000360	2·42	
N/9·38 Lactate	30°	0·000870	2·25	
	40°	0·00196		

Region in A°U.	Temperature	k_1 Monomolecular	True light reaction	Temperature co-efficient after deducting the dark reaction.	Quantum efficiency.
N/4·69 Sodium Lactate					
(5000-4450)	20°	0·000942	0·00022	2·02	9·23
Mean λ	30°	0·00224	0·00045	1·91	12·14
=4725	40°	0·00500	0·00086		16·37
(5850-5450)	20°	0·000862	0·000142	2·11	7·27
Mean λ	30°	0·00209	0·00030	2·03	11·75
=5650	40°	0·00475	0·00061		14·56
(7608-7000)	20°	0·000797	0·000077	2·21	3·97
	30°	0·00196	0·00017	2·06	6·52
Mean λ =7304	40°	0·00449	0·00035		8·38
N/9·38-*Sodium lactate* λ=4725	30°	...	...	...	6·8

Absorption—Sodium lactate N/4·69 and iodine N/100 in N/34·3 KI. 10 c.c. each.

Region in A°U.	7000	6707	5970	5670	5490	5320	5200
Extinction co-efficient.	·03	·05	·15	·17	·47	·55	·78
Region in A°U.	5000	4910	4800	4720	4670	4550	4400
Extinction Co-efficient	1·05	1·42	2·69	4	Beyond ∞	Complete absorption.	

4. *Sodium tartrate and iodine.*

One of us (*Proc. Akad. Wetensch. Amsterdam*, 1916, **24**, 974) observed that this reation is photosensitive. We have now determined the kinetics, temperature coefficients and energetics of this reaction in the dark and in radiations of different wave-lengths. The rate of reaction was followed by estimating the unchanged iodine by the thiosulphate. The experimental results are as follows :—

Sodium tartrate N/2·42 *and iodine* N/100 *in* N/34·3-KI, 10 *c.c. each.*

Dark.	Temperature.	k_1 Monomolecular	Temperature co-efficient.	Total order.
	20°	0·000378	2·51	
	30°	0·000948		
N/2·42-Tartrate	40°	0·00236	2·49	Bimolecular.
	20°	0·000189		
	30°	0·000473	2.5	
N/4·84-Tartrate	40°	0·00113	2·39	

Region in A°U.	Temperature.	k_1 Monomolecular	True light reaction.	Temperature co-efficient after deducting the dark reaction.	Quantum efficiency.
N/2·42 *Na-tartrate*					
(5000-4450)	20°	0·000554	0·000176		11·4
Mean λ	30°	0·00132	0·000372	2·11	13·7
=4725	40°	0·003107	0·000747	2·0	17·9
(5850-5450)	20°	0·000506	0·000128		8·6
Mean λ	30°	0·00123	0·000282	2·20	12·2
=5650	40°	0·00295	0·000590	2·09	13·7
(7608-7000)	20°	0·000451	0·000073		4·2
Mean λ	30°	0·001113	0·000165	2·26	7·1
=7304	40°	0·00272	0·000360	2·18	9·6
N/4·84 *Sodium tartrate* + N/100 *iodine*					
λ=4725	30°	...	...	...	6·8

Absorption:—*Sodium tartrate* N/2·42 *and iodine* N/100 *in* N/34·3 KI, 10 *c.c. each.*

Region in A°U	7000	6707	5970	5670	5490	5320	5200
Extinction co-efficient.	·04	·07	·19	·21	·50	·61	·89
Region in A°U.	5000	4910	4800	4720	4670	4550	4400
Extinction co-efficient.	1·08	1·5	2·75	4	Beyond scale	Tototal absorption.	Tototal absorption.

5. *Citric acid and Chromic acid.*

The kinetics, temperature coefficients and energetics of this and the two subsequent reactions have been investigated by us in sunlight (Bhattacharyya and Dhar, *Z. anorg. Chem.*, 1928, **169**, 381).

We have now determined the temperature coefficient and quantum efficiency of these reactions in radiations of different wavelengths. The results are as follows:—

Citric acid 6·75 N *and Chromic acid* N/44·4, 10 *c.c. each.*

Dark.	Temperature.	k_1 Monomolecular.	Temperature co-efficient.
	24°	0·000359	3·73
	34°	0·00134	
	44°	0·00485	3·65

Region in A°U.	Temperature	K, Monomolecular	True light reaction.	Temp. co-eff. after deducting the dark reaction.	Quantum efficiency.
(5000-4450)	24°	0·000610	0.000251	2·59	3·
Mean λ	34°	0·00191	0·000650		6·7
=4725	44°	0·00645	0·00160	2·46	8·2
	24°	0·00057	0·000211		2·7
(5850-5450)				2·66	
Mean λ	34°	0·00188	0·00054		4·8
=5650	44°	0·00622	0·00137	2·54	6·2
(7608-7000)	24°	0·000487	0·000128	2·89	1·5
Mean λ	34°	0·00171	0·00037		4·2
=7304	44°	0·00587	0·00102	2·75	5·2
3·375 N—*Citric acid* + N/44·4 *Chromic acid.*					
λ=4725	24°	...	...	...	1·8
3·375 N *Citric acid*					91
Sunlight	30°	...	...	...	129
	40°				159
	50°				

Absorption:—Citric acid 6·75 N *and Chromic acid* N/44·4, 10 *c.c. each.*

Region in A°U	7000	6707	5970	5670	5490	5320	5200
Extinction co-efficient	·04	·11	·13	·16	·18	·22	·38
Region in A°U	5000	4910	4800	4720	4670	4550	4400
Extinction co-efficient	·52	·53	·60	·65	·91	[illegible]	1·11

6. *Tartaric acid* N/4·27 *and Chromic acid* N/44·4, 10 *c.c. each.*

Dark.	Temperature.	k_1 Monomolecular	Temperature co-efficient.
	22°	0·00143	
			2·13
	32°	0·00305	
			2·04
	42°	0·00621	

Region in A°U.	Temperature.	k_1 Monomolecular.	True light reaction.	Temperature co-efficient after deducting the dark reaction.	Quantum efficiency.
(5000-4450)	22°	0·00174	0·00031		8·6
				1·9	
Mean λ	32°	0·00364	0·00059		12·7
				1·86	
=4725	42°	0·00731	0·00110		15·6
(5850-5450)	22°	0·00162	0·00019		7·4
				1·95	
Mean λ	32°	0·00342	0·00037		11·2
				1·9	
=5650	42°	0·00691	0·00070		14·2
(7608-7000)	22°	0·00154	0·00011		5·6
				2	
Mean λ	32°	0·00327	0·00022		8·3
				1·95	
=7304	42°	0·00664	0·00043		11·0
N/8·54 *Tartaric acid* + N/44·4 *Chromic acid.*					
λ=4725	22°	...	...	...	4·8
N/10·14 *Tartaric acid* + N/44·4 *Chromic acid.*					
	30°	...	...	...	76·4
Sunlight	40°	...	...	—	173
	50°	...	...	...	520

Absorption:—*Tartaric acid* N/4·27 *and Chromic acid* N/44·4 10 *c.c. each.*

Region in A°U.	7000	6707	5970	5670	5490	5320	5200
Extinction co-efficient.	·03	·10	·14	·16	·18	·24	·27
Region in A°U.	5000	4910	4800	4720	4670	4550	4400
Extinction co-efficient.	·48	·54	·61	·67	·83	·95	1

7. N/4·72 *Lactic acid and* N/44·8 *Chromic acid*, 10 *c.c. each.*

Dark.	Temperature.	k_1 Monomolecular.	Temperature co-efficient.
	22°	0·00108	
			1·8
	32°	0·00195	
			1·75
	42°	0·00341	

Region in A°U.	Temperature.	k_1 Monomolecular.	True light reaction.	Temperature co-efficient after deducting the dark reaction.	Quantium efficiency.
(5000-4450)	22°	0·00148	0·00040		2·8
				1·62	
Mean λ	32°	0·00260	0·00065		5·3
				1 57	
=4725	42°	0·00443	0·00102		7·6
(5850-5450)	22°	0·00136	0·00028		2·4
				1·7	
Mean λ	32°	0·00243	0·00048		4·6
				1·63	
=5650	42°	0·00419	0·00078		5·9
(7608-7000)	22°	0·00120	0 00012		1·8
				1·75	
Mean λ	32°	0·00216	0·00021		3·2
				1·7	
=7304	42°	0·00377	0·00036		4·6
N/9·44 *Lactic acid* + N/44 4 *Chromic acid*					
λ=4725	22°	...	...	...	1·8
N/4·72 *Lactic acid* + *Chomic acid* N/44·4.					
Sunlight	30°	...	...	...	23·6
	40°	...	...	...	32·12
	50°	...	...	...	84·84

Absorption:—N/4·72 *Lactic acid and* N/44·4 *Chromic acid*, 10 *c.c, each.*

Region in A°U.	7000	6707	5970	5670	5490	5320	5200
Extinction coefficient.	·03	·09	·13	·14	·17	·23	·27
Region in A°U.	5000	4910	4800	4720	4670	4550	4400
Extinction co-efficient.	·48	·52	·61	·65	·83	·93	1

Discussion.

From the results recorded in the foregoing pages it will be observed that the Einstein Law of photochemical equivalence is not exactly applicable to these reactions. In the bleaching of neocyanin the quantum efficiency varies from 1 to 5 at different temperatures. Hence this reaction does not deviate largely from Einstein's Law. In all cases so far investigated in these laboratories the quantum efficiency increases with temperature, and concentration of the reacting system and the frequency of the incident radiation.

Our experimental results show that in general the higher the temperature coefficient of a reaction in light, the greater is the ratio of the quantum efficiency at the same temperatures.

In a foregoing paper we have obtained very high quantum yields in the reactions between chromic acid and tartaric acid, chromic acid and lactic acid and chromic acid and citric acid in presence of sunlight and these values have been recorded in this paper for comparison with those obtained with the radiations $\lambda=4725$ Å, $\lambda=5650$ Å and $\lambda=7304$ Å It will be at once evident that the quantum yield is much greater in sunlight than in radiations of wavelength $\lambda=4725$ Å, $\lambda=5650$ Å and $\lambda=7304$ Å. Exactly similar results have been obtained with other reactions in these laboratories. The quantum yield for the hydrogen-chlorine reaction and the decomposition of ammonia in white light is much greater than that obtained by the summed reaction of the different parts of the spectrum (compare Kuhn, *Compt. rend.*, 1923, **177**, 956).

The experimental results show that in all cases the temperature coefficient of the photochemical changes are less than those of the corresponding thermal reactions. The greater the acceleration in light of different wave-lengths, the less the temperature coefficient.

The bleaching of neocyanin is accelerated most by radiation of $\lambda=7304$ Å and least by radiation $\lambda=4725$ Å and the temperature coefficient in presence of radiations of $\lambda=7304$ Å is 1·12 and in light of $\lambda=4725$ Å it is 1·29.

Another interesting fact is that the temperature coefficient of the purely light reaction is always greater than unity and in some cases as high as 2·59 (chromic acid and citric acid) and 2·5 (decomposition of ferric thiocyanate). Values of temperature coefficients much higher than unity have been obtained in more than 30 photochemical

reactions investigated in these laboratories. Hence the generally accepted view that the temperature coefficient of photochemical reaction is unity is not true.

It is believed that photochemical reactions are brought about only by violet and ultra-violet radiations. Our results, however, prove that chemical changes can be accelerated by radiations of wave-length $\lambda = 7304$ Å which lies in the infra-red region of the spectrum. We have been able to accelerate more than thirty reactions by radiations $\lambda = 7304$ Å. From measuremenss of extinction coefficients of these reacting mixtures we find that there is appreciable absorption in the region $\lambda = 7000$ Å and this absorption leads to acceleration of the reaction. The extinction coefficient of neocyanin shows that radiations of wave-lengths longer than $\lambda = 5670$Å are completely absorbed even by very dilute solutions of neocyanin. As the wave-length of the incident radiation is decreased the absorption passes through a minimum and then increases with the decrease of wave-length. The velocity of the bleaching of neocyanin is greatest in the region $\lambda = 7304$Å, less in the region $\lambda = 5650$ Å and least in the region $\lambda = 4725$Å. This shows that the velocity of the reaction and absorption go hand in hand.

We have measured photographically the absorption of several of these reacting mixtures using a Hilger quartz spectrograph with a copper arc as the source of light. With an exposure of about 2 minutes no absorption is observed with mixtures of chromic acid and organic acids in the region of wave-lengths greater than $\lambda = 4275$Å, but our experimental results on the velocity measurements show that these reactions are not only accelerated by radiations of wave-length $\lambda = 4725$Å and $\lambda = 5650$Å which lie in the visible part of the spectrum but even by $\lambda = 7304$ Å which lie in the infra-red region. It appears therefore that small amount of absorption of incident light cannot be observed by photographic method on short exposure.

Summary.

(1) The decomposition of ferric thiocyanate is unimolecular in light. The temperature coefficients are:—2·12 (4725 Å); 2·3 (5650 Å); 2·5 (7304 Å). The quantum yield varies from 4 to 12.

(2) The bleaching of neocyanin in light is unimolecular. The temperature coefficients are:—1·29 (4725 Å); 1·2 (5650Å); 1·12 (7304 Å). The quantum yield varies from 1 to 5.

(3) The reaction between sodium lactate and iodine is bimolecular in light and in the dark. The temperature coefficieuts are:—2·49 (dark); 2·02 (4725Å); 2·11 (5650Å) ; 2·21 (7304Å) The quantuml yield varies from 4 to 16.

(4) The reaction between sodium tartrate and iodine is bimolecular in light and in the dark. The temperature coefficients are:—2·51 (Dark); 2·11 (4725Å); 2·2 (5650Å); 2·26 (7304Å). The quantum yield varies from 4 to 18.

(5) The temperature coefficients of the reaction between chromic and citric acids are:—3·73 (dark); 2·59 (4725Å) ; 2·66 (5650Å); 2·89 (7304Å). The quantum yield varies from 2 to 8, but in sunlight it is abnormally high.

(6) The temperature coefficients of the reaction between chromic and tartaric acids are:—2·13 (dark); 1·9 (4725Å) ; 1·95 (5650Å); 2 (7304Å). The quantum yield is much higher than that demanded by the law of photochemical equivalence.

(7) The temprature coefficients of the reaction between chromic and actic acids are:—1·8 (dark); 1·62 (4725Å) ; 1·7 (5650Å); 1·75 (7304Å). The quantum yield varies from 2 to 8.

(8) The quantum yield increases with the concentrations and temperature of the systems and the frequency of the incident radiations.

(9) All these reactions are accelerated by radiations of wavelength 7304Å, which lies in the infra-red region.

(10) Extinction coefficient measurements with all these reacting systems, show that there is appreciable absorption of radiations of wave-length 7000Å and this absorption leads to the acceleration of the reactions.

(11) Chemical reactions can be accelerated by infra-red radiations.

(12) The temperature coefficients of these photochemical reactions are greater than unity. The greater the observed acceleration of a reaction by light, the less is the temperature coefficient.

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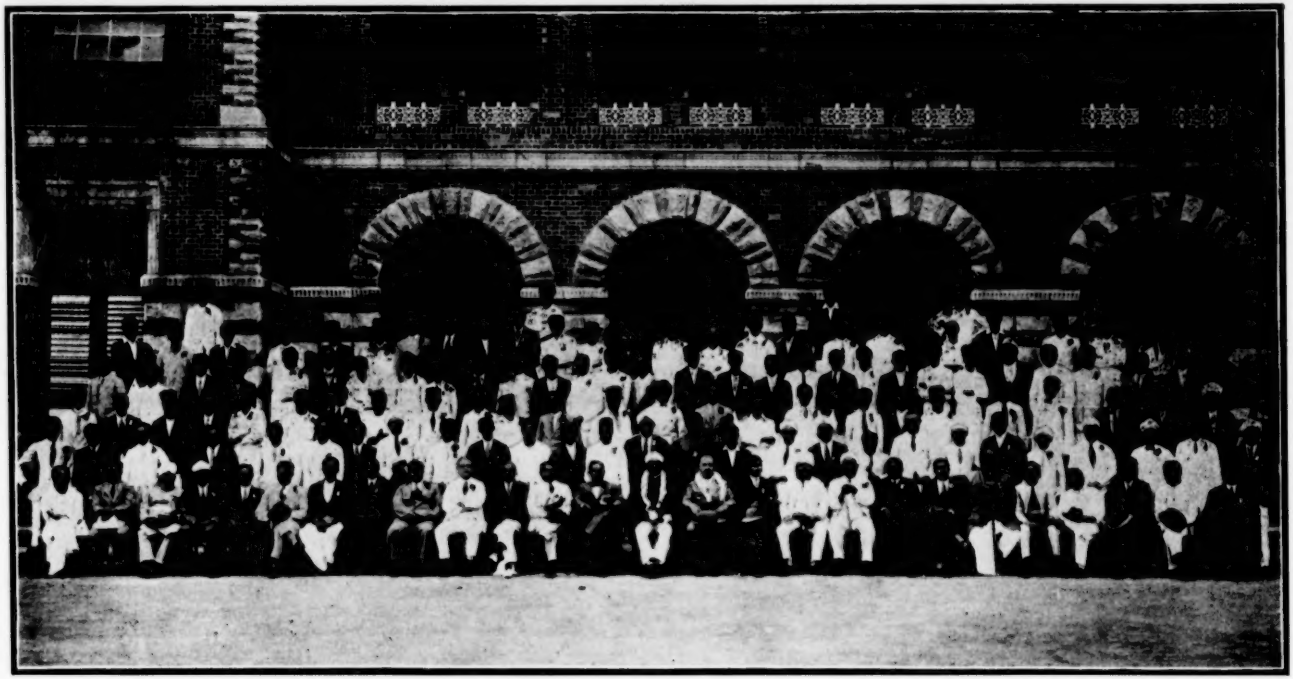

The Fifth Annual General Meeting of the Indian Chemical Society, held in Madras, January, 1929.

The Behaviour of Hemolytic Serum, Complement-free Hemolytic Serum and Normal Serum in presence of Chemical Hemolysers.

By Kshitish Chandra Sen and Narendra Nath Mitra.

In a previous paper we have studied the hemolytic behaviour of mixtures of hemolytes. It was stated there that in an early paper Moore, Wilson and Hutchinson (*Biochem. J.*, 1909, **4**, 346) studied the effect of hemolytic pig serum on the hemolytic action of some soaps and found a retardation of hemolysis. In our previous paper we have shown that when two chemical hemolytes are used in a mixture, the total effect is almost additive. Since no detailed study of the behaviour of a hemolytic serum in presence of other chemical hemolytes has yet been made, it was thought desirable to make a thorough investigation of the subject. This paper contains an experimental study of the behaviour of hemolytic serum in presence of saponin, oleate, taurocholate, acid and alkali. A comparative study has also been made of the effects of hemolytic serum and the same serum from which the complement has been destroyed. The effect of normal serum in causing the inhibition or acceleration of hemolysis has also been very thoroughly investigated.

Experimental.

The method of experimentation is almost the same as given in our previous papers. Human serum has been used as the hemolytic serum in these experiments. This serum normally contains hemolysins for sheep corpuscles (compare Effront, "Biochemical Catalysts in Life and Industry," English Translation, 1917, p. 466). The human serum has been used in a dilution of 1 in 10. All solutions were made in saline.

Experiments with hemolytic serum.

In the following tables, the results with hemolytic serum will be given. The corpuscle concentration in every case is 0·2 per cent. of which 1 c.c. has been used each time. The total volume is 4 c.c. In Table I the hemolytic efficiency of the pure human serum on sheep corpuscles is shown.

TABLE I.

Amount of human serum 1/10 in c. cm.	1·0	1·2	1·4	1·6	1·8	2·0	2·2	2·4
Time of hemolysis in minutes.	30	22	18½	15½	13	12	11	10

It was observed soon that the hemolytic efficiency of the human serum considerably diminished on standing for a few days. Consequently fresh serum had to be used often and the hemolytic titre was not the same for every serum. In Table II the effect of hemolytic serum on saponin hemolysis is shown. The concentration of saponin is 1 in 10,000.

TABLE II.

Amount of saponin in c.c.	Time in minutes of hemolysis in presence of hemolytic serum,—c.c. 0·0	0·1	1·0
0·0	—	—	8½
0·6	26	—	—
0·7	20¾	—	—
0·8	13½	No hemolysis in 2 hours.	—
0·9	11¼	Partial hemolysis in 2 hours.	—
1·0	9	70	10¾
1·1	6¼	16	10¾
1·2	3	12	10½

In Tables III, IV, V and VI the results with oleate, taurocholate, acid and alkali are shown. The oleate concentration is 1 in 50,000, the taurocholate concentration is 0·1 per cent., acid concentration N/500 and the concentration of alkali is N/25. Other conditions remain the same.

TABLE III.

Amount of oleate in c.c.	Time in minutes of hemolysis in presence of hemolytic serum,—c.c.		
	0·0	0·1	1·0
0·0	—	—	8½
0·8	20	No hemolysis in 2 hrs.	9
0·9	11½	Do.	—
1·0	10	Do.	9
1·1	6½	Do.	—
1·2	5½	5% hemolysis in 2 hrs.	9

TABLE IV.

Amount of taurocholate in c.c.	Time in minutes of hemolysis in presence of hemolytic serum—c.c.		
	0·0	0·1	1·0
0·0	—	—	8½
0·4	21	No hemolysis in 1½ hrs.	—
0·6	4½	5% hemolysis in 1½ hrs.	—
0·8	2½	30% hemolysis in 1½ hrs.	—
1·0	1½	80% hemolysis in 1½ hrs.	13½

TABLE V.

Amount of HCl in c.c.	Time in minutes of hemolysis in presence of hemolytic serum—c.c.		
	0·0	0·1	1·0
0·0	—	—	14
0·4	14½	60% hemolysis in 1 hr.	—
0·6	5	24	—
0·8	4	8½	—
1·0	3	3	70% hemolysis in 1 hr.
1·2	2	2	40% hemolysis in 1 hr.

TABLE VI.

Amount of NaOH in c.c.	Time in minutes of hemolysis in presence of hemolytic serum—c.c.		
	0·0	0·1	1·0
0·0	—	—	11
0·4	9	16¼	—
0·6	6	10¾	—
0·8	4¼	8	—
1·1	3½	6¼	11½
1·2	2¾	5	—

From the above tables it will be apparent that though hemolytic serum can itself hemolyse the corpuscles quite easily in proper concentrations, yet its presence in low concentration has a markedly inhibiting effect on hemolysis by taurocholate, oleate, saponin, acid and alkali. When present in comparatively greater amounts, it appears that apparently its action is almost independent of the presence of the chemical hemolytes whose hemolytic efficiency seems to be altogether inhibited. This will be evident from the tables with oleate and saponin, where it will be found that with 1 c.c. of hemolytic serum and with 1 and 1·2 c.c. of the hemolytes, the time of hemolysis is practically identical with the result obtained when no chemical hemolytes are present. This will be further evident from the fact that a mixture of 1 c.c. saponin and 2 c.c. hemolytic serum required 5 minutes for complete hemolysis while 2 c.c. of the same serum alone took the same time for hemolysis. This shows that at higher concentrations of the hemolytic serum, the effect of oleate or saponin is probably completely inhibited by a very small quantity of the serum and the final effect actually observed is due to the excess of serum alone. A slightly different result is obtained with taurocholate where a greater inhibition is observed. With acid the effect is also similar, but with alkali a slightly different result is obtained, namely, that the effect of mixtures with higher concentrations of serum is slightly greater than that of serum alone. With a low concentration of hemolytic serum however, a markedly inhibiting action on hemolysis by alkali was observed.

A comparative study of the effects of hemolytic serum and complement-free serum.

In the foregoing tables we have shown that soaps, saponin etc., are antagonistic to hemolytic serum. Many years ago Sachs and Altmann (*Ber. Klin. Wochenschr.*, 1908, pp. 494, 699) first observed this inhibiting effect of sodium oleate on hemolytic serum and considered that the effect of sodium oleate was due to an anti-complement action on the hemolytic serum. Our results which extend considerably that of Sachs and Altmann show that this phenomenon of inhibition is a general one and Moore and coworkers (*loc. cit.*) have already given reasons for considering that the view of Sachs and Altmann cannot be upheld. In the following tables we shall compare the effect of an hemolytic serum with a complement-free serum. For these results a portion of the hemolytic serum was heated for half an hour at 56° to destroy its complement. This inactivated serum was then tested and found to have lost its hemolytic power altogether. In the following tables the effect of this complement-free serum is compared to that of the normal hemolytic serum.

TABLE VII.

Amount of saponin, 1/5000.	Time of hemolysis without serum.	Time in minutes of hemolysis in presence of 0·1 c.c.	
		Hemolytic serum.	Complement-free hemolytic serum.
1·5 c.c.	10½	34½	29
2·0 ,,	6½	11	14½
2·5 ,,	2½	5½	6½

TABLE VIII.

Amount of taurocholate 0·1%.	Time of hemolysis without serum.	Time of hemolysis in presence of 0·1 c.c.	
		Hemolytic serum.	Complement free-serum.
1·5 c.c.	7	Slight hemolysis in ½ hour	Slight hemolysis in ½ hour
2·0 ,,	3½	10½	13
2·5 ,,	1½	5	6½

From these two tables it will be evident that excepting one datum with saponin which may be due to some error, the general results show that the complement-free serum has a greater inhibiting action than the pure serum. The general nature of the results is also the same with low concentrations of the serums whether the complement has been destroyed or not.

Effect of normal serum on the hemolysis by chemical hemolytes.

In a previous paper (Sen and Sen, this *Journal*, 1928, **5**, 261) we discussed some results of Ponder (*Proc. Roy. Soc.*, 1923, **95**, B, 403) on the acceleration of taurocholate hemolysis by normal serum. It was shown by us that contrary to the results obtained by Ponder, an acceleration of taurocholate hemolysis could be observed when normal serum was added to a mixture of taurocholate and corpuscles under the experimental conditions of concentration, etc., used by us ; and that Ponder's results might have been obtained under some special conditions. Ponder (private communication) has suggested to us recently that the results obtained by us are perfectly correct for the particular concentrations of the reacting substances used by us and that an acceleration can only be obtained under certain concentration ranges. Since no detailed study of this acceleration and inhibition of hemolysis in presence of normal serum has yet been published by anybody, we thought it desirable to make a thorough study of the problem; but we desire to express at this place our thanks to Dr. Ponder of the New York University for his valuable suggestions. A study of the literature shows that it is probably Sachs (*Biochem. Zeit.*, 1908, **12**, 278) who first observed this phenomenon of acceleration of hemolysis by oleate in presence of normal serum. Since this acceleration and retardation of hemolysis by normal serum must be of great theoretical importance, we shall give our results in some details. In the following experiments, the concentration of cells is 1 per cent., taurocholate 0·3 per cent , total volume 5 c.c. and the dilution of the serum is 1 in 10. The quantity of the corpuscles, the quantity of the hemolyte as well as the amount of serum has been varied in different experiments. All the experiments have been done in normal saline.

TABLE IX.

2 C. c. corpuscles are used in each experiment.

Experiments.	Time of hemolysis.
1. 2 C. c. taurocholate + 1 c. c. saline added 1/2 minute after the addition of taurocholate.	3 mins. 2 secs.
2. 2 C. c. taurocholate + 1 c. c. serum added 1/2 minute after the addition of taurocholate.	56% hemolysis in 1 hr.
3. 1·5 c. c. taurocholate + 1·5 c. c. saline added 1/2 minute after the addition of taurocholate	17 mins. 18 secs.
4. 1·5 c. c. taurocholate + 1·5 c.c. serum added 1/2 minute after the addition of taurocholate.	No hemolysis in 1 hr.

TABLE X.

1·0 C. c. cells and 0·5 c. c. taurocholate have been used in each experiment. The time of complete hemolysis of the blank is 7 mins. 20 secs.

Amount of serum added in c.c.	Time of complete hemolysis in presence of—	
	Serum added together with taurocholate.	Serum added 1/2 minute after the addition of taurocholate.
0·1	122 mins.	57 mins. 46 secs.
0·2	66% hemolysis in 3½ hours	63 ,, 0 ,,
0·3	—	45 ,, 11 ,,
0·4	—	18 ,, 54 ,,
0·5	No hemolysis in 4 hours	1 ,, 42 ,,
0·6	—	0 ,, 54 ,,
0·7	—	0 ,, 47 ,,

TABLE XI.

1·0 C.c. cells and 1 c.c. taurocholate have been used in each experiment. The time of complete hemolysis of the blank when 0·5 c.c. saline was added 1/2 minute after the addition of taurocholate was 1 min. 18 secs.

Amount of serum added in c.c.	Time of complete hemolysis in presence of—	
	Serum added together with the taurocholate.	Serum added 1/2 minute after the addition of taurocholate.
0·1	4 mins. 6 secs.	3 mins. 29 secs.
0·2	44 ,, 0 ,,	4 ,, 23 ,,
0·3	No hemolysis in 2 hrs.	1 ,, 43 ,,
0·4	—	1 ,, 23 ,,
0·5	—	1 ,, 7 ,,

TABLE XII.

0·5 C.c. cells and 0·5 c.c. taurocholate have been used in each experiment. The time of complete hemolysis of the blank was 3 mins. 21 secs.

Amount of serum added in c.c.	Time of complete hemolysis in presence of—	
	Serum added together with the taurocholate.	Serum added 1/2 minute after the addition of taurocholate.
0·1	16 mins. 16 secs.	14 mins. 46 secs,
0·2	No hemolysis in 1/2 hr.	22 ,, 28 ,,
0·5	—	1 ,, 4 ,,
1·0	—	0 min. 32 ,, (immediate hemolysis).

In the following experiments the concentration of corpuscles is 0·2 per cent. and taurocholate concentration is 0·1 per cent. Both the solutions were fresh.

TABLE XIII.

1·0 C.c. cell and 0·5 c.c. taurocholate have been used in each experiment. The time of hemolysis of the blank is 11 mins. 31 secs.

Amount of serum added in c.c.	Time of hemolysis when serum is added ½ minute after the addition of hemolyte.
0·03	35 mins. 35 secs.
0·05	90% hemolysis in 2½ hrs.
0·10	50% hemolysis in 2½ hrs.
0·15	80% hemolysis in 2½ hrs.
0·20	1 min. 0 sec.
0·30	0 min. 37 secs.

There was practically no hemolysis in the blank experiment in half a minute.

So long the results with taurocholate hemolysis have been given. In the following tables the results obtained in oleate hemolysis will be given. The concentration of corpuscles is 1 per cent. and the oleate concentration is 1 in 10,000. Other conditions remain the same.

TABLE XIV.

1·0 C.c. cell and 1·0 c.c. oleate have been used each time. The time of hemolysis of the blank experiment when 1·0 c.c. saline was added ½ minute after the addition of oleate is 2 mins. 52 secs.

Amount of serum added in c.c.	Time of hemolysis in presence of—	
	Serum added together with the hemolyte.	Serum added ½ minute after the addition of hemolyte.
0·1	10 mins. 56 secs.	10 mins. 48 secs.
0·2	—	21 mins. 50 secs.
0·3	10% hemolysis in 1 hr.	70% hemolysis in 1 hr.
0·4	No hemolysis in 1 hr.	50% hemolysis in 1 hr.
0·5	No hemolysis in 1 hr.	70% hemolysis in 2½ hrs.
1·0	—	90% hemolysis in 2 hrs.

In these experiments, in majority of cases where serum was added to the mixture of hemolyte and corpuscles, hemolysis started

within a few minutes and about 60 per cent. hemolysis was finished within several minutes in certain cases but the rate then became very slow. A similar fact has also been noticed in the experiments given in Table XV, where with higher concentrations of the serum, almost 90 per cent. of hemolysis was finished within a few minutes after the addition of the serum but then the progress became very slow.

TABLE XV.

0·5 C.c. cells and 0·5 c.c. oleate are used each time. The time of hemolysis of the blank experiment when 2 c.c. saline was added 1 minute after the addition of the hemolyte is 7 mins. 59 secs.

Amount of serum added in c.c.	Time of hemolysis in presence of: Serum added together with the hemolyte.	Serum added 1 minute after the addition of hemolyte.
0·2	No hemolysis in 1 hour	5% hemolysis in 1 hour.
0·5	—	52 mins. 54 secs.
1·0	—	68 ,, 45 ,,
2·0	—	8 ,, 0 ,,

TABLE XVI

0·2 c.c. cells used each time.

Experiment.	Time of hemolysis.
1. 0·3 c.c. oleate + 1 c.c. saline added ½ minute after addition of oleate.	9 mins. 10 secs.
2. 0·3 c.c. oleate + 1 c.c. serum added together with the oleate.	20% hemolysis in 1 hour.
3. 0·3 c.c. oleate + 1 c.c. serum added ½ minute after addition of oleate.	25% hemolysis in 1 hour.
4. 0·5 c.c. oleate + 1 c.c. saline added 1 minute after addition of oleate.	5 mins. 8 secs.
5. 0·5 c.c. oleate + 1 c.c. serum added 1 minute after addition of oleate.	3 ,, 26 ,,
6. 0·5 c.c. oleate + 2 c.c. saline added 1 minute after addition of oleate.	3 ,, 8 ,,
7. 0·5 c.c. oleate + 2 c.c serum added 1 minute after addition of oleate.	1 ,, 58 ,,
8. 0·6 c.c. oleate + 1 c.c. saline added 1 minute after addition of oleate.	2 ,, 35 ,,
9. 0·6 c.c. oleate + 1 c.c. serum added 1 minute after addition of oleate.	1 ,, 53 ,,

In the following Table XVII, some further experimental results on the effect of normal serum on oleate hemolysis is shown. The corpuscle concentration is 0·2 per cent. and oleate 1 in 10,000. The solutions were made from fresh samples. 1 C.c. cell and 0·3 c.c. oleate have been used each time. When 1 c.c. saline was added to the blank experiment 1 minute after the addition of the oleate, the time of complete hemolysis was 6 mins. 9 secs.

TABLE XVII.

Amount of serum added in c.c.	Time of hemolysis when serum is added 1 minute after the addition of hemolyte.	Remarks.
0·1	146 mins.	No appreciable hemolysis on the addition of serum.
0·2	210 mins	
0·3	180 mins.	
0·4	6 mins. 42 secs.	
0·5	5 mins. 54 secs.	Hemolysis starts on the addition of serum in all these cases.
0·6	5 ,, 1 sec.	
0·7	4 ,, 1 sec.	
0·8	3 ,, 28 secs.	
0·9	3 ,, 19 secs.	
1·0	3 ,, 10 secs.	

In the following Table XVIII, some data will be given showing the effect of the time-interval after which the serum is added to the corpuscle and hemolyte mixture on the observed acceleration of hemolysis.

TABLE XVIII.

Experiment.	Time of hemolysis.	Remarks.
1. 0·5 c.c. oleate + 1 c.c. saline added 1 minute after oleate.	3 mins. 24 secs.	No appreciable hemolysis after 1 minute.
2. 0·5 c.c. oleate + 1 c.c. serum added ½ minute after oleate.	10 ,, 1 sec.	Hemolysis does not start on the addition of serum but takes an appreciably long time.
3. 0·5 c.c. oleate + 1 c.c. serum added 1 minute after oleate.	1 ,, 3 secs.	Hemolysis is practitally finished as soon as serum is added.

In the following tables, the results in saponin hemolysis are shown. The corpuscle concentration is 1 per cent. and the saponin concentration is 1 in 1,000:—

TABLE XIX.

1·0 C.c. cell used in each experiment.

Experiment.	Time of hemolysis.
1. 0·2 c.c. saponin + 1 c.c. saline added ½ minute after saponin.	43 mins. 24 secs.
2. 0·2 c.c. saponin + 1 c.c. serum added together with the serum.	5% hemolysis in 4 hours.
3. 0·2 c.c. saponin + 1 c.c. serum added ½ minute after saponin.	30% hemolysis in 4 hours.
4. 0·4 c.c. saponin + 0·5 c.c. saline added ½ minute after saponin.	13 mins. 10 secs.
5. 0·4 c.c. saponin + 0·5 c c. serum added together with saponin.	27 ,, 49 ,,
6. 0·4 c.c. saponin + 0·5 c.c. serum added ½ minute after saponin.	20 ,, 24 ,,
7. 0·4 c.c. saponin + 1 c.c. saline added ½ minute after saponin.	12 ,, 0 sec.
8. 0·4 c.c. saponin + 1 c.c. serum added together with saponin.	57 ,, 43 secs.
9. 0·4 c.c. saponin + 1 c.c. serum added ½ minute after saponin.	38 ,, 50 ,,
10. 1 c.c. saponin + 1 c.c. saline added ½ minute after saponin.	1 ,, 20 ,,
11. 1 c.c. saponin + 1 c.c. serum added ½ minute after saponin.	1 ,, 28 ,,

TABLE XX.

0·5 C.c. cells used in each experiment.

Experiment.	Time of hemolysis.
1. 0·3 c.c. saponin + 1 c.c. saline added ½ minute after saponin.	9 mins. 5 secs.
2. 0·3 c.c. saponin + 1 c.c. serum added together with saponin.	80% hemolysis in 1½ hours.
3. 0·3 c.c. saponin + 1 c.c. serum added ½ minute after saponin.	61 mins. 0 sec.
4. 0·3 c.c. saponin + 0·5 c.c. serum added together with saponin.	24 ,, 31 secs.
5. 0·3 c.c. saponin + 0·5 c.c. serum added ½ minute after saponin.	21 ,, 45 secs.

TABLE XXI.

0·2 C.c. cells used in each experiment.

Experiment.	Time of hemolysis.
1. 0·2 c.c. saponin + 0·5 c.c. saline added ½ minute after saponin.	13 mins. 21 secs.
2. 0·2 c.c. saponin + 0·5 c.c. serum added together with saponin.	70% hemolysis in 40 mins.
3. 0·2 c.c. saponin + 0·5 c.c. serum added ½ minute after saponin.	70% hemolysis in 40 minutes.
4. 0·2 c.c. saponin + 1 c.c. serum added ½ minute after saponin.	50% hemolysis in 40 mins.
5. 0·3 c.c. saponin + 1 c.c. saline added 1/2 minute after saponin.	4 mins. 54 secs.
6. 0·3 c.c. saponin + 1 c.c. serum added 1/2 minute after saponin.	70% hemolysis in 20 mins.

In the following Table XXII two data are shown with very small amount of corpuscles. 0·2 C.c. cells of a 0·2% corpuscle suspension have been used in these experiments. Other conditions remain the same ; the solutions were prepared fresh.

TABLE XXII.

1. 0·3 c c. saponin + 1 c.c. saline added 1 minute after saponin.	3 mins. 41 secs.
2. 0·3 c.c. saponin + 1 c,c. serum added 1 minute after saponin.	25% hemolysis in 50 minutes

Discussion.

The results given above may be conveniently divided for the present into two groups ; in one of which comes taurocholate and oleate and in the other, saponin. It will be noticed from the results that up till now no acceleration of saponin hemolysis could be observed in presence of normal serum whether it be added before or after the addition of saponin. Thus though the corpuscle concentration and the hemolyte concentration have been varied within wide limits and the amount of serum actually added has been varied to a great extent, no acceleration of hemolysis has been observed. With taurocholate and oleate however, the results are different. With comparatively higher concentration of the corpuscles, it has been found in agreement with our previously published results, that

no acceleration of hemolysis could be observed by normal serum whether it be added before or after the addition of the hemolytes. When however the corpuscle concentration decreases, normal serum appears to have two effects on the corpuscle + hemolyte system. In low concentrations, it still inhibits the hemolysis, but as the concentration of the serum increases the time taken for complete hemolysis passes through a maximum and in some cases becomes smaller than the time necessary for hemolysis in the absence of any serum. In other words, an actual acceleration of hemolysis by normal serum is to be observed under these conditions. These results thus confirm the observations of Sachs and Ponder on oleate and taurocholate hemolysis. The importance of our results however lies on the fact that we have, for the first time, obtained a complete curve of this inhibition and acceleration of hemolysis with the increase in the amount of serum under comparative conditions. Thus from Fig. I, in which the results given in Table XII are graphically plotted and which is a representative curve in the whole series of results, it will be observed that when

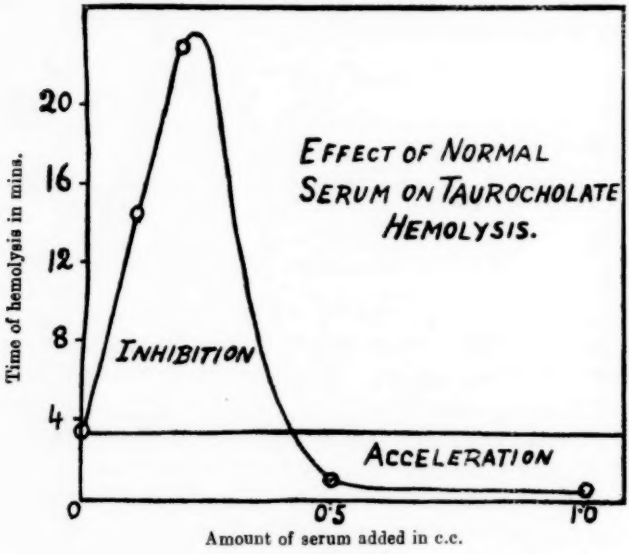

Fig. I

the concentration of the cells, the hemolyte, as well as the time-interval of the addition of serum remain constant, there is a fairly wide concentration range of the serum in which we get only an

inhibition of hemolysis. When the concentration of serum exceeds this limit an acceleration of hemolysis is obtained. A similar phenomenon is also to be observed in oleate hemolysis. It will also be observed from the results given in Table XVIII that the time interval after which the serum is added to the corpuscle and hemolyte mixture is of great importance in some cases for obtaining an acceleration of hemolysis. Thus it will be noticed from these results that with an interval of half a minute only, no acceleration could be observed, whereas, when the time-interval was one minute, an acceleration of hemolysis could be easily obtained. Identical results have also been obtained in experiments done in a solution of sucrose which form the subject matter of another paper. Our study on the effect of normal serum on taurocholate and oleate hemolysis therefore leads us to the conclusion that the addition of normal serum to the red blood cells before the hemolyte is actually added always inhibits the hemolysis ; whereas when serum is added after the addition of the hemolyte, we may get either an inhibition or an acceleration of hemolysis depending on the particular concentrations of the red blood cells, the hemolytes, the amount of serum added and in certain cases, on the time-interval after which the serum is added to the mixture of corpuscle and hemolyte. Attention may also be drawn here to the fact, remarked sometimes in the tables, that when serum was added to the corpuscle and hemolyte mixture, often the hemolysis started immediately on the addition of the serum and as much as 80% or near about of hemolysis was finished within three or four minutes. The remaining 20% of hemolysis, however, took in many cases more than several hours to be complete. In the blank experiments in which no serum was added or only a small amouut of serum was added, there was no appreciable hemolysis within the first three or four minutes. But when the hemolysis actually started, it was finished fairly quickly. These effects were very often observed and the phenomena should be investigated in details.

Summary.

(1) An experimental investigation has been made on the hemolytic behaviour of chemical hemolytes like saponin, taurocholate, oleate, acid and alkali in presence of a hemolytic serum.

(2) It has been found that in low concentrations, hemolytic serum behaves qualitatively in a similar way to normal serum,

namely, it has an inhibiting effect on hemolysis by these chemical hemolytes. In higher concentrations, however, hemolytic serum has itself a hemolysing action and though neutralises almost completely the effect of these chemical hemolytes, it still retains its own hemolytic efficiency to a certain extent. This probably shows that only a small percentage of the serum is used up for inhibiting the action of the chemical hemolytes.

(3) A comparative study has been made of the inhibiting effect of hemolytic serum and the same serum from which the complement has been destroyed. It has been observed that the complement-free serum has a greater inhibiting action on hemolysis but unlike the other, it has no hemolytic action at higher concentrations.

(4) A detailed study has been made of the effect of normal serum on taurocholate, oleate and saponin hemolysis. It has been observed that when normal serum is added to the corpuscles either before the addition of the hemolytes or together with hemolytes, an inhibition of hemolysis is always observed. When, however, the serum is added to a mixture of hemolyte and corpuscles, either an inhibition or an acceleration of hemolysis can be obtained depending on the particular concentrations of the corpuscles, the hemolytes, the amount of serum added, and in certain cases, on the time-interval after which the serum is added to the mixture of corpuscle and hemolyte. This acceleration phenomenon has been observed in the case of taurocholate and oleate hemolysis but in the case of saponin hemolysis, we have up till now failed to get any acceleration and in every case an inhibition of hemolysis has been found.

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Hemolysis in Sucrose Solution and the Behaviour of Normal Serum in Presence of Chemical Hemolytes.

By Amaresh Chandra Roy and Kshitish Chandra Sen.

In a recent paper in this *Journal* (Sen and Mitra, 1929, **6**, 111), it has been shown that some abnormality in the time-dilution curve of taurocholate hemolysis is observed when comparatively higher concentrations of the corpuscles and the hemolyte are used. The time-dilution curve is however quite normal when lower concentrations are used. It will be remembered that an abnormal behaviour was also observed by MacLean and Hutchinson (*Biochem. J.*, 1909, **4**, 369) with glycocholate, choleate and cholalate. All these experiments have been made in saline. In a recent paper we have shown (Roy and Sen, this *Journal*, 1929, **6**, 89) that when experiments are done in sucrose solutions, sucrose appeared to have a greatly inhibiting action on taurocholate, oleate and saponin hemolysis. Since much investigation has not been carried out on hemolysis in sucrose solution, it was thought desirable to investigate the nature of the time-dilution curves of different hemolytes in sucrose, and specially that of taurocholate, to find out whether any abnormality in higher concentrations can be observed or not. An investigation has also been made of the effect of normal serum in presence of oleate and taurocholate in sucrose.

Experimental.

The experiments given in this paper have been done with sheep's corpuscles. The corpuscles were defibrinated in the usual way and then completely washed by repeated centrifuging with isotonic sucrose solution. The hemolytes used in this paper, namely, taurocholate, oleate and saponin were also prepared in sucrose. The normal serum used in these experiments was also diluted with sucrose solution. The method of experimentation is practically the same as given in previous papers from these laboratories. Different concentrations of the corpuscles and the hemolytes have been used and in the following tables the results are given. The total volume in every case has been 5 c.c. One c.c. of corpuscle suspension has been used in each experiment.

TABLE I.

Concentration of corpuscles = 5 per cent.
Taurocholate concentration = 3 ,,

Amount of taurocholate in c.c.	Final concentration.	Time of complete hemolysis.
0·1	1/1,666	47 mins. 53 secs.
0·3	1/555	7 mins. 37 secs.
0·4	1/416	4 mins. 30 secs.
0·5	1/333	2 mins. 6 secs.
1·0	1/166	0 min. 40 secs.
1·5	1/111	0 min. 49 secs.
2·0	1/83·3	1 min. 13 secs.
2·5	1/66·6	1 min. 12 secs.
3·0	1/55·6	1 min. 4 secs.
3·5	1/47·6	0 min 56 secs.

TABLE II.

Concentration of corpuscles = 1·0 per cent.
Taurocholate concentration = 0·3 ,,

Amount of taurocholate in c.c.	Final concentration.	Time of complete hemolysis.
0·3	1/5,555	50% hemolysis in two hours.
0·5	1/3,333	61 mins. 32 secs.
0·8	1/2,083	43 mins. 9 secs.
1·0	1/1,666	9 mins. 53 secs.
1·2	1/1,389	4 mins. 24 secs.
1·5	1/1,111	3 mins. 39 secs.
2·0	1/833	1 min. 30 secs.
2·5	1/666	1 min. 27 secs.

TABLE III.

Concentration of corpuscles = 0·2 per cent.
Taurocholate concentration = 0·1 ,,

Amount of taurocholate in c.c.	Final concentration.	Time of complete hemolysis.
0·1	1/50,000	No hemolysis in 40 minutes.
0·3	1/16,666	80% hemolysis in 40 ,,
0·5	1/10,000	23 mins. 45 secs.
0·6	1/8,333	12 mins. 11 secs.
0·7	1/7,143	7 mins. 39 secs.
0·8	1/6,250	5 mins. 50 secs.
1·0	1/5,000	4 mins. 21 secs.
1·5	1/3,333	2 mins. 57 secs.
2·0	1/2,500	2 mins. 18 secs.
2·5	1/2,000	1 min. 49 secs.

From these three Tables I, II, and III, it will be observed that in high concentrations, taurocholate gives an abnormal time-dilution curve in sucrose solution. This behaviour is however not so striking as was observed in the case of saline, which may be due to different conditions affecting the experiments. In low concentrations, however, there is no abnormality in the time-dilution curves and the results are quite similar to those obtained in saline solution. In the following tables some data with saponin hemolysis are shown.

TABLE IV.

Concentration of corpuscles = 5 per cent.
Saponin concentration = 1 in 1,000.

Amount of saponin in c.c.	Final concentration.	Time of complete hemolysis.
0·1	1/50,000	No hemolysis in 4 hours.
0·3	1/16,666	50% hemolysis in 4 hours.
0·5	1/10,000	25 mins. 58 secs.
0·6	1/8,333	19 mins. 21 secs.
0·8	1/6,250	5 mins. 24 secs.
1·0	1/5,000	3 mins. 47 secs.
1·2	1/4,166	2 mins. 28 secs.
1·5	1/3,333	1 min. 46 secs.
2·0	1/2,500	0 min. 58 secs.

TABLE V.

Concentration of corpuscles = 1·0 per cent.
Saponin concentration = 1 in 1,000.

Amount of saponin in c.c.	Final concentration.	Time of complete hemolysis.
0·1	1/50,000	No hemolysis in 3 hours.
0·2	1/25,000	30% hemolysis in 3 hours.
0·3	1/16,000	27 mins. 4 secs.
0·4	1/12,500	7 mins. 58 secs.
0·5	1/10,000	4 mins. 32 secs.
0·6	1/8,333	3 mins. 24 secs.
0·7	1/7,143	2 mins. 40 secs.
0·8	1/6,250	1 min. 51 secs.
0·9	1/5,555	1 min. 34 secs.
1·0	1/5,000	1 min. 8 secs.

TABLE VI.

Concentration of corpuscles = 0·2 per cent.
Saponin concentration = 1 in 5,000.

Amount of saponin in c.c.	Final concentration.	Time of complete hemolysis.
0·5	1/50,000	40% hemolysis in 2 hours.
0·8	1/31,250	67 mins. 30 secs.
1·0	1/25,000	36 mins. 6 secs.
1·2	1/20,833	8 mins. 58 secs.
1·5	1/16,666	6 mins. 23 secs.
2·0	1/12,500	5 mins. 44 secs.
2·5	1/10,000	3 mins. 38 secs.
3·0	1/8,333	3 mins. 1 sec.

From Tables IV, V, and VI, it will be observed that in every case no abnormality is to be observed in the time-dilution curves of saponin hemolysis. In the following tables results with oleate hemolysis are shown.

TABLE VII.

Concentration of copuscles = 5 per cent.
Oleate concentration = 1 in 10,000.

Amount of oleate in c.c.	Final concentration.	Time of complete hemolysis.
1·5	1/33,333	166 mins. 50 secs.
2·0	1/25,000	146 mins. 48 secs.
2·5	1/20,000	131 mins. 16 secs.
3·0	1/16,666	112 mins. 20 secs.
3·5	1/14,286	109 mins. 56 secs.

TABLE VIII.

Concentration of copuscles = 1·0 per cent.
Oleate concentration = 1 in 10,000.

Amount of oleate in c.c.	Final concentration.	Time of complete hemolysis.
1·0	1/50,000	14 mins. 41 secs.
1·5	1/33,333	12 mins. 10 secs.
2·0	1/25,000	11 mins. 18 secs.
2·5	1/20,000	10 mins. 38 secs.
3·0	9/16,666	9 mins. 46 secs.
3·5	1/14,286	8 mins. 58 secs.
4·0	1/12 500	8 mins. 7 secs.

TABLE IX.

Concentration of corpuscles = 0·2 per cent.
Oleate concentration = 1 in 10,000.

Amount of oleate in c.c.	Final concentration.	Time of complete hemolysis.
0·1	1/500,000	28 mins. 18 secs.
0·2	1/250,000	15 mins. 37 secs.
0·3	1/166,666	12 mins. 17 secs.
0·5	1/100,000	10 mins. 39 secs.
0·8	1/62,500	8 mins. 8 secs.
1·0	1/50,000	6 mins. 55 secs.
1·5	1/33,333	6 mins. 10 secs.

From the above tables it will be quite apparent that hemolysis in sucrose solutions shows in all important respects an almost identical behaviour to that carried in saline solutions. Thus an abnormal behaviour is obtained in the case of taurocholate in a particular concentration range whereas in other concentration of taurocholate as well as with other hemolytes like oleate and saponin a perfectly normal behaviour is observed. These results are quite comparable to those obtained in saline solutions; the only difference when absolutely comparable data are obtained is an inhibiting effect on the hemolytic efficiency of these hemolytes by sucrose.

Effect of normal serum in presence of taurocholate and oleate.

In a previous paper from this laboratory, (Sen and Sen, this *Journal*, 1928, **5**, 161) it was shown with reference to certain work on the retardation and acceleration of hemolysis in presence of normal serum that under ordinary conditions of the experiments carried out by us, no acceleration of taurocholate hemolysis could be observed in presence of normal serum. Since then a large amount of experiments have been carried out by us on this subject, an account of which is being communicated simultaneously with this paper.

It has been shown there that an acceleration of hemolysis can be observed in presence of serum only under certain special conditions. Since all those experiments have been done in saline solutions, it was thought interesting to investigate the behaviour of normal serum in sucrose solution also. This is also necessary because in the former paper by Sen and Sen (*loc. cit.*) many results were obtained in sucrose solutions. In the following tables, the results obtained have been given.

In these tables the concentration of corpuscles is 0·2 per cent. of which 1 c.c. has been used each time. The taurocholate concentration is 0·1 per cent. and serum is 1 in 10.

TABLE X.

Experiment.	Time of hemolysis.
1. 0·5 c.c. taurocholate	4 mins 26 secs.
2. 0·5 c.c. taurocholate + 0·5 c.c. serum added ½ minute after the addition of taurocholate	50% hemolysis in 1½ hours.

Experiment.	Time of hemolysis.
3. 0·5 c.c. taurocholate + 1 c.c. serum added $\frac{1}{2}$ minute after the addition of taurocholate	70% hemolysis in 1½ hours.
4. 0·5 c.c. taurocholate + 1 c.c. serum added 1 minute after the addition of taurocholate	26 mins. 33 secs.*

TABLE XI.

1 C.c. taurocholate has been used in each experiment.
Time of hemolysis of the blank experiment with taurocholate =2 mins. 20 secs.

Amount of serum added each time in c.c.	Time of complete hemolysis in presence of serum added half a minute after the addition of taurocholate.
0·1	12 mins. 20 secs.
0·2	30% hemolysis in 1 hour
0·3	5% hemolysis in 1 hour
1·0	12 mins. 56 secs.

TABLE XII.

1 C.c. taurocholate used each time.
Time of hemolysis of the blank experiment=2 mins. 20 secs.

Amount of serum added each time in c.c.	Time of hemolysis in presence of serum added 1 minute after the addition of taurocholate.
0·1	7 mins. 4 secs.
0·2	2 mins. 54 secs.
0·3	2 mins. 10 secs.
0·4	1 min. 26 secs.
0·5	1 min. 3 secs.
1·0	Immediate hemolysis.

In the following tables, the results obtained in oleate hemolysis are shown. The concentration of corpuscles is 0·2 per cent. of which 1 c.c. has been used each time. Oleate concentration is 1 in 5,000.

TABLE XIII.

0·5 C.c. oleate used in each experiment.

Time for hemolysis of the blank experiment = 6 mins. 40 secs.

Amount of serum added each time in c c.	Time of complete hemolysis in presence of different amounts of serum —added together with oleate.	—added one minute after oleate.
0·1	7 mins. 40 secs.	6 mins. 45 secs.
0·2	21 mins. 16 secs.	8 mins. 11 secs.
0·3	—	1 min. 21 secs.
0·4	—	Almost immediate hemolysis.

TABLE XIV.

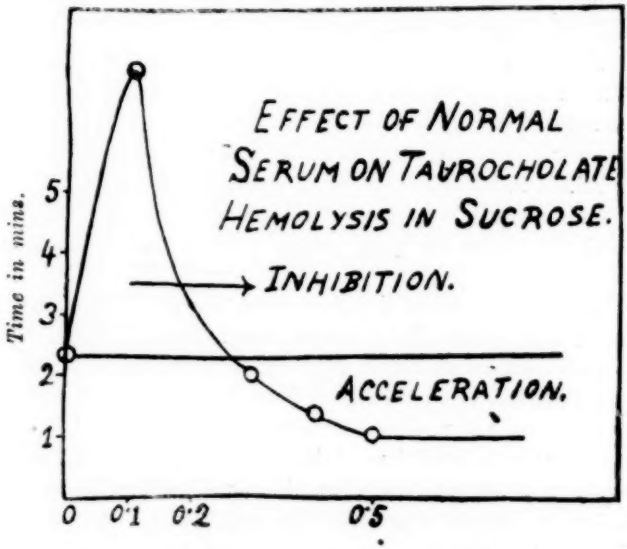
1·0 C.c. oleate used in each experiment.

Time for hemolysis of the blank experiment = mins. 24 secs.

Amount of serum added each time in c.c.	Time of complete hemolysis in presence of different amounts of serum —added together with oleate.	—added one minute after oleate.
0·1	6 mins. 38 secs.	4 mins. 48 secs.
0·2	8 mins. 16 secs.	1 min. 23 secs.
0·3	13 mins. 3 secs.	1 min. 6 secs.

It will be observed from Table X that when the concentration of taurocholate is 0·5 c.c. and the serum is added half a minute after the addition of taurocholate, the effect of serum is always a retarding one. This agrees with the results obtained by Sen and Sen previously in which all the experiments showed a retarding effect of normal serum in taurocholate hemolysis. Entirely similar behaviour is to be observed in Table XI with one c. c. taurocholate. Marked difference is however to be noticed in the results given in Table XII where both retardation and acceleration of hemolysis are to be observed with one c. c. taurocholate, the only difference in the experimental conditions of Tables XI and XII being an increase in the time-interval of addition of normal serum from half a minute to one minute. These results therefore show the great influence of the time-interval after which the serum is added to the mixture of corpuscles and hemolyte in certain cases. Another thing to be noticed in this connection in Table XII is the fact that when the

concentration of serum added is low, an inhibition of hemolysis is observed when the serum is added to the mixture of taurocholate and corpuscles, but when the serum concentration is comparatively higher, an acceleration of hemolysis is observed. From the data of Sen and Sen previously published and confirmed by us, it has been found that with higher concentration of corpuscles, no acceleration of hemolysis can be obtained in presence of serum, and in every case there is a retardation. Similar results have also been observed in the case of oleate hemolysis. In Fig. I, the results given in Table XII are graphically shown, from which it will be observed that with



Amount of serum added in c.c.

Fig. I.

increase in the addition of serum after a certain time-interval, a continuous curve of inhibition and acceleration can be obtained. Since acceleration and inhibition is theoretically very important, a complete mathematical analysis of curves of this nature is desirable. Since it has been shown that the amount of corpuscles, amount of serum, etc., has a great effect on this observed acceleration of hemolysis, we can summarise our conclusions by saying that in sucrose solution the effect of normal serum is quite analogous to that in saline solutions and inhibition or acceleration

of hemolysis by normal serum, when it is added to a mixture of taurocholate or oleate and corpuscles, depends upon the particular concentration of the corpuscles, concentration of the serum, concentration of the hemolyte and the time-interval after which the serum is added. These conclusions are absolutely similar to those arrived at from our study in saline solutions.

Summary.

1. An experimental study of hemolysis of sheep's corpuscles has been made in sucrose solutions by taurocholate, saponin and oleate in presence or absence of normal serum.

2. It has been observed that in taurocholate hemolysis abnormal time-dilution curves are obtained with comparatively higher concentration of corpuscles and hemolyte. With lower concentrations however, the results are quite normal and in these respects sucrose solutions behave in an analogous way to the saline solutions.

3. With saponin and oleate, the time-dilution curves are all normal and the results are quite similar to those obtained in saline solutions.

4. When normal serum is added before the addition of any of the hemolytes or a mixture of normal serum and the hemolyte is added to the corpuscles an inhibition in hemolysis is observed. When the serum is added to a mixture of corpuscle and taurocholate or oleate either an inhibition or an acceleration can be observed depending on the particular conditions of the experiment. An acceleration of hemolysis may be observed when the concentration of the corpuscle is low, the amount of serum is high and the time interval after which the serum is added to the corpuscle and hemolyte mixture is comparatively greater. In all important respects experiments done in saline as well as in sucrose solutions show similar results.

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Lengthened *ortho*-Di-derivatives of Benzene and their Ring-closure: Formation of Polymembered Heterocyclic Compounds from Substituted Phenylenedicarbamides.

By Tejendra Nath Ghosh and Praphulla Chandra Guha.

The ring-closing action of hydrochloric acid, sodium hydroxide and acetic anhydride upon hydrazine-dicarbon-mono- and -di-thioamides has been studied in some details and a large number of thiodiazole and triazole derivatives have been obtained (Freund, *Ber.*, 1895, **28**, 946; 1896, **29**, 2506; Arndt and co-workers, *Ber.*, 1921, **54**, 2089; 1922, **55**, 341; Fromm, *Annalen*, 1923, **433**, 1; *Monatsch*, 1924, **44**, 298; *Ber.*, 1923, **56**, 1370; Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502; 1923, **45**, 1036; 1925 **47**, 387). It was thought worthwhile to extend the field of such dicarbonamides so as to comprise the corresponding —CO-NHR and —CS-NHR derivatives of aromatic and aliphatic 1:2-diamines. Phenylene and ethylene-diamines, it is well known, form dithiocarbamides with ammonium sulphocyanide which readily form phenylene or ethylene-thioureas. The following mixed and simple disubstituted dicarbamides as also the mono- and di-thiocarbamide * have now been prepared from *ortho*-phenylene or *o*-tolylenediamines.

$C_6H_4(NH\text{-}CS\text{-}NH\text{-}Ph)_2$ (I)

$C_6H_4(NH\text{-}CS\text{-}NH\text{-}C_6H_4.CH_3)_2$ (*o*- and *p*-) (II, III)

$C_6H_4(NH\text{-}CS\text{-}NH\text{-}C_6H_3(CH_3)_2)_2$ (IV)

$CH_3.C_6H_3(NH\text{-}CS\text{-}NHPh)_2$ (V)

$C_6H_4(NH\text{-}CS\text{-}NH\text{-}CH_3)_2$ (VI)

$C_6H_4(NH\text{-}CS\text{-}NH\text{-}C_3H_5)_2$ (VII)

$$C_6H_4\begin{cases}NH—CS—NH—Ph\\NH—CS—NH\cdot C_3H_5\end{cases}$$ (VIII)

* Compounds I, VII, XV are known (*Annalen*, 1885, **228**, 200, 201, Ber. 1883, **16**, 592) but no unsymmetrically substituted mono or dithio-dicarbamide is known.

(IX, X)

(XI)

(XII)

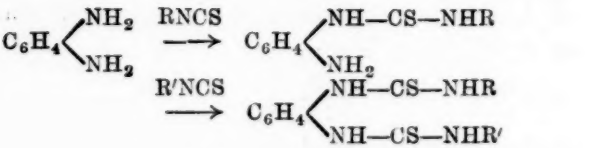
(XIII)

(XIV)

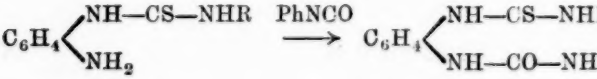
(XV)

(XVI)

The unsymmetrically substituted dithiocarbonamides VIII, IX, and X have now been obtained by the action of one molecule of mustard oil upon the monomustard oil compounds of the diamine, thus:

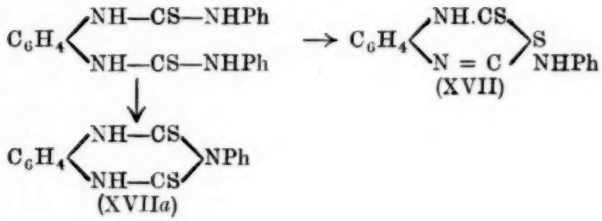


whereas, the monothiodicarbonamides XI, XII, XIII and XIV have been prepared by the action of phenyl *iso*cyanate upon the monomustard oil compounds of the diamine, thus:

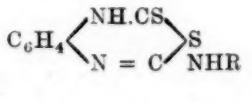


o-Phenylene-diphenyldithiocarbamide (I) loses a molecule of aniline on being heated with strong hydrochloric acid or 20 % potassium hydroxide solution. The elimination of aniline might take place in either of the following two different manners forming 2-anilino-4:5-benzo-7-thioketo-1:3:6-heptathiodiazine (XVII) or

1-*N*-phenyl-2:7-dithioketo-4:5-benzo-1:3:6-heptatriazine (XVII*a*), thus:



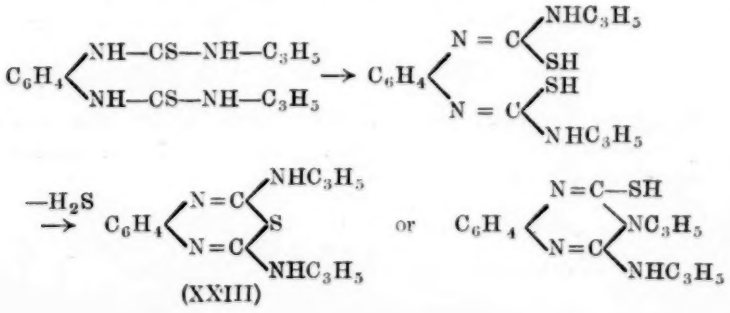
The compound actually isolated behaves like a mono-mercaptan as it has been found that for disulphide formation two molecules of the substance require only two atomic proportions of iodine (compare Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502). So, the dimercaptanic formula has been rejected. The other disubstituted dithiocarbamides (II-VI and VIII-X) behave similarly as the diphenyl compound to yield substituted amino-heptathiodiazines XVII—XXII, XXIV—XXVI respectively.



R=Ph, XVII; *o*-tolyl, XVIII; *p*-tolyl, XIX; xylyl, XX; Me XXII; C_3H_5, XXIV; XXV=XVIII; XXVI=XIX.

It is significant that although in compounds VIII, IX, and X the two thiocarbamide groupings are substituted by two different groups (*viz.*, $C_6H_5:C_3H_5$, $C_6H_5:o\text{-}C_6H_4\cdot CH_3$, $C_6H_5:p\text{-}C_6H_4\cdot CH_3$) aniline is invariably eliminated in each case.

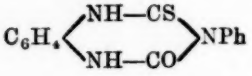
The behaviour of *o*-phenylene-diallyl-dithio-carbamide (IX) is peculiar and instead of allylamine one molecule of sulphuretted hydrogen is eliminated with the formation of 2:7-diallylamino-4:5-benzo-1:3:6-thioheptadiazine, XXIII, thus:



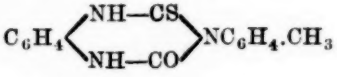
the alternative formula has been rejected on the ground of its showing no mercaptanic properties and also because of the fact that it forms a diacetyl derivative from which no acetyl group can easily be knocked out by hydrolysis as would have been the case with an acetylthiol compound (*vide* Guha, *ibid*). Acetic anhydride brings about the same type of ring-closure yielding the diacetyl derivative of XXIII which can be deacetylated only by boiling with strong hydrochloric acid. This peculiar behaviour of the allyl compounds, *viz.*, favouring the formation of sulphur-containing rings will also be noticed in the case of mono-allyl-thio-carbonamide, XXXVI.

The action of strong hydrochloric acid has been studied on the four phenylene mono-thio-dicarbamides XI, XII, XIII and XIV with the result that they have been found to yield quite different types of compounds from those obtained from the compounds containing dithio-carbamide groupings.

Compounds XI and XII, which are substituted by aryl groups, give 1-*N*-phenyl-2-keto-4:5-benzo-7-thioketo-1 : 3 : 6-heptatriazine (XXVII) and 1-*N*-tolyl-2-keto-4:5-benzo-7-thioketo-1:3:6-heptatriazine (XXVIII) respectively.

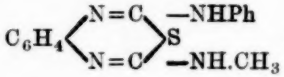


(XXVII)

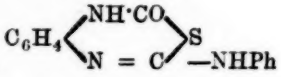


(XXVIII)

The mono-thio-dicarbamide (XIII) yields with the loss of one molecule of water 2-methylamino-4:5-benzo-7-phenylamino-1:3:6-thioheptadiazine (XXIX), whereas from (XIV) there is obtained 2-phenylamino-4:5-benzo-7-keto-1:3:6-thio-heptadiazine (XXX).

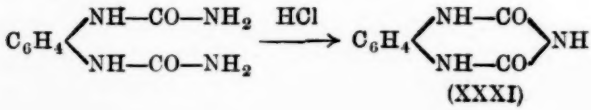


(XXIX)



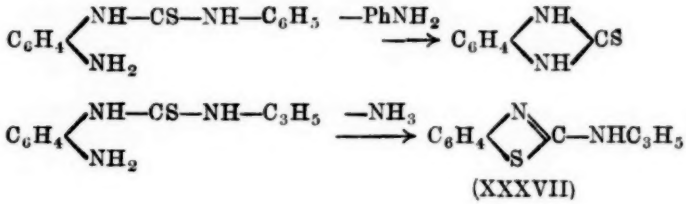
(XXX)

Phenylene diurea (XV) yields phenylene biuret (XXXI), whereas the corresponding diphenyl substituted compound (XVI) remains unaffected by the action of hydrochloric acid.



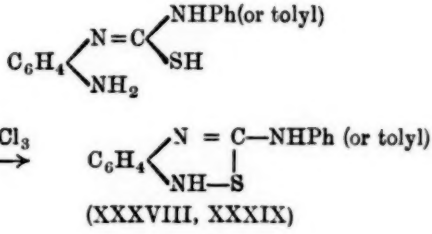
(XXXI)

The first four of the following five mono-mustard oil compounds of *o*-phenylene-diamine, *viz.*, NH_2-C_6H_4-NH-CS-NHPh (XXXII), NH_2-C_6H_4-NH-CS-NH-C_6H_4-CH_3 (*ortho* and *para*) (XXXIII and XXXIV), NH_2-C_6H_4-NH-CS-NH-CH_3 (XXXV) and NH_2-C_6H_4-NH-CS-NH-C_3H_5 (XXXVI) react with strong hydrochloric acid to yield *o*-phenylene-thiourea, evidently with the elimination of the respective amines, whereas, the last one behaves in a quite different manner to yield 5-allylamino-2:3-benzo-1:4-thiazole (XXXVII), thus:



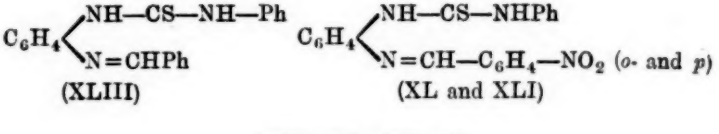
(XXXVII)

A suitable reagent for the building up of arylamino-benzo-thiodiazine compounds has been found in ferric chloride which acting upon (XXXII) and (XXXIV) gives rise to 3:4-benzo-6-anilino-1:2:5-thiodiazine (XXXVIII) and 3:4-benzo-6-*p*-tolylamino-1:2:5-thiodiazine (XXXIX) respectively thus:

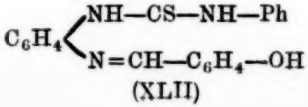


(XXXVIII, XXXIX)

The free amino groups of the mono-mustard oil compounds of phenylene diamine react readily with aldehydes to yield—

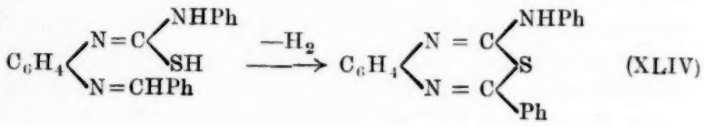


(XLIII) (XL and XLI)



(XLII)

of which the first one has been oxidised by ferric chloride to 2-phenyl-4:5-benzo-7-anilino-1:3:6-heptathiodiazine (XLIV), thus:



(XLIV)

Experimental.

2-Phenylamino-4 : 5-phenylene-7-thioketo-1:3 : 6-thioheptadiazine (XVII).—*o*-Phenylene-diphenyl-dithiocarbamide (2 g.) (prepared according to the method given in *Annalen*, 1885, **228**, 200) was heated under reflux with hydrochloric acid 65 c.c. (*d* 1.19) for about half an hour when a green solution mixed with some tarry matter was obtained. On further heating for 15 minutes, the tarry mass solidified. The reaction mixture was allowed to cool and the green precipitate was filtered, washed with water and finally crystallised from water acidulated with a few drops of hydrochloric acid in beautiful white rectangular plates, m.p. 290°-291°. It can be precipitated by acid from a caustic soda solution. Yield 1·1 gms. (Found: S 22·61. $C_{14}H_{11}N_3S_2$ requires S, 22·45 per cent.). The presence of aniline in the acid filtrate was proved.

The acetyl derivative.—The above compound (0·5 g.) was heated with about 5 c.c. of acetic anhydride under reflux for about 15 minutes, when a perfectly clear solution was obtained, which, on being poured into cold water, yielded a white crystalline mass. It was further crystallised from acetic acid, m.p. 160°.

The Disulphide.—Iodine solution (in potassium iodide) was added drop by drop to an alcoholic solution of the above thio-compound (XVII) and gently warmed. On dilution with water it gave a yellowish amorphous mass which was washed free from excess of iodine with potassium iodide solution, water and finally with alcohol ; m.p. 210°. (0·067 Gm. of the substance required 0·0312 gm. of iodine for oxidation. $C_{14}H_{11}N_3S_2$ with one thiol group present in it requires 0·03 gm. of iodine ; with two thiol groups it requires 0·06 gm. of iodine).

Action of caustic potash solution on o-phenylene-diphenyl-dithiocarbamide: *Formation of Compound* (XVII).—*o*-Phenylene-diphenyl-dithi-ocarbamide (2 g.) was heated under reflux with an excess of potassium hydroxide solution (20%) for about 2 hours when a clear solution was obtained. The solution after cooling was acidified with hydrochloric acid when a white solid came down with slight evolution of sulphuretted hydrogen. The white precipitate after filtration was crystallised from hot water acidulated with a few drops of hydrochloric acid ; m.p. 290-291°. It is soluble in cold dilute alkali and is precipitated by acids. It gives an insoluble mercaptide with mercuric chloride and a disulphide (m.p. 210°) with iodine. (Found: S, 22·59. $C_{14}H_{11}N_3S_2$ requires S, 22·45 per cent.). Evidently, this compound is identical with the compound (XVII) as obtained on treatment with hydrochloric acid. This fact was further confirmed by taking the mixed melting point.

o-*Phenylene-di*-o-*tolyl-dithiocarbamide* (II).—An alcoholic solution of *o*-phenylene diamine (2·1 g.) was heated under reflux on the water-bath with *o*-toly! mustard oil (3 g.) for about half an hour when a white crystalline precipitate was obtained, which was recrystallised from alcohol ; m.p. 161°. Yield is almost quantitative. (Found: S, 15·62. $C_{22}H_{22}N_4S_2$ requires S, 15·76 per cent.).

2-o-*Tolylamino*-4:5-*phenylene*-7-*thioketo*-1:3:6-*thio-heptadiazine* (XVIII).—Two gms. of the above compound (II) were heated under reflux with hydrochloric acid 60 c.c. (*d* 1·19) for about 30 minutes when a green solution mixed with some tarry matter was obtained. On further heating, the tarry mass solidified. The precipitate after filtration was crystallised from alcohol ; m.p. 300°. (Found: S, 21·31. $C_{15}H_{13}N_3S_2$ requires S, 21·40 per cent.).

The *acetyl* derivative was crystallised from acetic acid; m.p. 200°.

o-*Phenylene-di*-p-*tolyl-dithiocarbamide* (III).—The method of preparation was the same as in the case of the preceding compound (II). The yield was almost quantitative. It was crystallised from alcohol in shining white plates, m.p. 178°. (Found: S, 15·82. $C_{22}H_{22}N_4S_2$ requires S, 15·76 per cent.).

2-p-*Tolylamino*-4:5-*phenylene*-7-*thioketo*-1:3:6-*thio-heptadiazine* (XIX).—The method of preparation was the same as in the case of the preceding compounds (XVII and XVIII). It was crystallised from alcohol ; m.p. 300.° It is soluble in cold dilute alkali from

which it is precipitated by acids. (Found: S, 21·26. $C_{15}H_{13}N_3S_2$ requires S, 21·40 per cent.). The *disulphide* of the above compound was prepared as in the case of the corresponding phenyl compound; m.p. 190.° (0·206 Gm. of the substance required 0·088 gm. of iodine for oxidation: $C_{15}H_{13}N_3S_2$ containing one thiol group requires 0·087 gm. of iodine).

The *acetyl* derivative was obtained in the usual way and was crystallised from acetic acid ; m.p. 200.°

o-*Phenylene-di*-(1 : 3 : 4)-*xylyl-dithiourea* (IV).—The method of preparation was the same as in the case of the corresponding phenyl and tolyl compounds. It was crystallised from alcohol ; m.p. 145°. (Found: S, 14·39. $C_{24}H_{26}N_4S_2$ requires S, 14·74 per cent.).

Action of strong hydrochloric acid upon (IV): *Formation of* 2-(1 : 3 : 4)-*xylylamino*-4 : 5-*phenylene*-7-*thioketo*-1 : 3 : 6-*thioheptadiazine* (XX).—It was prepared similarly as the compounds (XVII, XVIII, XIX) and was crystallised from alcohol; m.p. 295°. It is soluble in cold dilute alkali from which it can be precipitated by acids. It gave an amorphous disulphide (m.p. 172°) with iodine solution. (Found: S, 20·13. $C_{16}H_{15}N_3S_2$ requires S, 20·44 per cent.).

The *acetyl* derivative was crystallised from acetic acid ; m.p. 296°.

o-*Toluylene-diphenyl-dithiocarbamide* (V).—An alcoholic solution of *o*-toluylene diamine (1·2 g.) was heated under reflux on the water-bath with phenyl mustard oil (2·7 g.) for about 30 minutes when a white crystalline precipitate was obtained which was crystallised from alcohol; m. p. 142°. Yield is almost quantitative. (Found: S, 16·48. $C_{21}H_{20}N_4S_2$ requires S, 16·32 per cent.).

Action of strong hydrochloric acid upon (V): *Formation of* 2-*Phenylamino*-4 : 5-*methylbenzo*-7-*thioketo*-1 : 3 : 6-*thioheptadiazine* (XXI).—The above compound (V, 2 g.) was heated under reflux with concentrated hydrochloric acid (60 c.c.) for about half an hour when a green solution was obtained. The solution, on cooling, deposited a solid which was crystallised from alcohol, m. p. 265°. It is soluble in cold dilute alkali from which it is percipitated by acids. (Found: N, 14·21. $C_{15}H_{13}N_3S_2$ requires N, 14·04 per cent.). The presence of aniline in the acid filtrate was proved. The *disulphide* was prepared in the usual way ; m. p. 137°.

The *acetyl* derivative was crystallised from acetic acid, m. p. 185°.

o-Phenylene-dimethyl-dithiocarbamide (VI).—Phenylene-diamine (3 g.) was dissolved in alcohol to which methyl mustard oil (4 g.) was added and the solution was boiled for sometime. The clear solution, on cooling, gave colourless crystals which were recrystallised from alcohol, m. p. 175°. (Found: S, 24·85. $C_{10}H_{14}N_4S_2$ requires S, 25·19 per cent.).

2-*Methylamino*-4 : 5-*benzo*-7-*thioketo*-1 : 3 : 6-*thioheptadiazine* (XXII).—Two grams of the compound (VI) were boiled with strong hydrochloric acid (65 c.c.) for about 2 hours. The solution, when cold, gave a white crystalline mass which was further crystallised from alcohol ; m. p. 168°. It is soluble in cold alkali from which it is precipitated by acids. (Found: N, 19·15. $C_9H_9N_3S_2$ requires N, 18·83 per cent.).

The *disulphide* was prepared in the usual manner, m. p. 194°.

2:7-*Diallylamino*-4:5-*benzo*-1:3:6-*thioheptadiazine* (XXIII).—Three gms. of *o*-phenylene-diallyl-thiourea (VII) (prepared according to the method given in *Annalen*, 1885, **228**, 201) were heated with strong hydrochloric acid (70 c.c.) under reflux for about 30 minutes when a greenish coloured clear solution was obtained. The cold solution, on dilution with water, gave no precipitate. However, on making the solution alkaline with ammonia a white solid mixed with some tarry matter was obtained, and was purified by dissolving in dilute hydrochloric acid and precipitated by ammonia. It was finally crystallised from acetone, m. p. above 300°. (Found: N, 20·37. $C_{14}H_{16}N_4S$ requires N, 20·58 per cent.).

Action of acetic anhydride upon o-*Phenylene-diallyldithiocarbamide*: *Formation of diacetyl compound of* (XXIII).—*o*-Phenylene-diallyl-dithiourea (2 g.) was heated with 10 c. c. of acetic anhydride under reflux for about 45 minutes when a clear solution was obtained, which on cooling, gave a crystalline mass. It was further crystallised from acetic acid in slender white needles, m. p. 185°. (Found: N, 16·11. $C_{18}H_{20}N_4S$ requires N, 15·73 per cent.).

Deacetylation of the above compound was effected by boiling with strong hydrochloric acid for about half an hour when a

clear solution was obtained, which, on being made alkaline, gave a white precipitate which crystallised from acetone, m. p. above 300°. (Found: N, 20·39. $C_{14}H_{16}N_4S$ requires N, 20·58 per cent.).

o-*Phenylene*-sym.-*phenylallyl-dithiourea* (VIII).—An alcoholic solution of 1-*o*-aminophenyl-3-phenyl-thiocarbamide (2·5 g.) and allyl mustard oil (1 g.) was heated on the water-bath under reflux for about 2 hours. The reaction product was then allowed to cool when a crystalline mass separated out which was further crystallised from alcohol, m. p. 245°. (Found: S, 18·48. $C_{17}H_{18}N_4S_2$ requires S, 18·71 per cent.)

2-*Allylamino*-4:5-*benzo*-7-*thioketo*-1:3:6-*thioheptadiazine* (XXIV).—Two gms. of the compound (VIII) were heated with strong hydrochloric acid (50 c. c.) under reflux for about an hour. The solution turned red with the separation of a solid which crystallised from alcohol, m. p. 293°. It is soluble in cold dilute alkali from which it can be precipitated by acids. The presence of aniline in the acid filtrate was proved. (Found: N, 16·58. $C_{11}H_{11}N_3S_2$ requires N, 16·86 per cent.).

The *disulphide* was prepared in the usual manner, m. p. above 300°.

o-*Phenylene*-sym-*phenyl*-o-*tolyl-dithiourea* (IX).—An alcoholic solution of 1-*o*-amino-phenyl-3-phenyl-thiocarbamide (2·4 g.) and *o*-tolyl-mustard oil (1·5 g.) was heated on the water-bath under reflux for about 2 hours. The reaction-product on cooling gave a solid which crystallised from alcohol; m. p. 136° (Found: S, 16·59. $C_{21}H_{20}N_4S_2$ requires S, 16·32 per cent.)

2-o-*Tolylamino*-4: 5-*phenylene*-7-*thioketo*-1 : 3:6-*thioheptadiazine* (XXV).—Two gms. of the compound (IX) were heated with strong hydrochloric acid (50 c.c.) under reflux for about an hour when a clear solution was obtained. This, on being further heated, gave a solid mass which was crystallised from alcohol; m. p. 300°. It is soluble in cold alkali from which it is precipitated by acids. The presence of aniline in the acid filtrate was proved. (Found: N, 14·31. $C_{15}H_{13}N_3S_2$ requires N, 14·04 per cent.) Identity of this compound with the compound (XVIII) was further confirmed by taking the mixed melting point.

o-*Phenylene*-sym.-*phenyl*-p-*tolyl-dithiourea* (X).—The method of preparation was the same as in the case of the compound (IX). The substance was crystallised from alcohol; m. p. 165°. (Found: S, 16·48. $C_{21}H_{20}N_4S_2$ requires S, 16·32 per cent.).

2-p-*Tolylamino*-4:5-*phenylene*-7-*thioketo*-1:3: 6-*thioheptadiazine* (XXVI).—The method of preparation was the same as in the case of the compound (XXV). The substance was crystallised from alcohol; m. p. 300°. (Found: N, 14·28. $C_{15}H_{13}N_3S_2$ requires N, 14·04 per cent.). The identity of this compound with (XIX) was further confirmed by taking a mixed melting point.

1-*Phenyl-carbamido*-2-*phenyl-thiocarbamido-benzene* (XI).—An alcoholic solution of 1-*o*-aminophenyl-3-phenyl-thiocarbamide (2·4 g.) and phenyl *iso*cyanate (1·2 g.) was heated for about 30 minutes when a white solid separated out which crystallised from alcohol, m. p. 200° (after shrinking at 140°). (Found: N, 15·27. $C_{20}H_{18}ON_4S$ requires N, 15·46 per cent.).

1-*Phenyl*-2-*keto*-4:5-*benzo*-7-*thioketo*-1: 3-6-*heptatriazine* (XXVII).—Two gms. of the compound (XI) were heated under reflux with concentrated hydrochloric acid (60 c.c.) for about 2 hours when a solid mass with a greenish coloured mother-liquor was obtained. The solid was filtered, washed with water and crystallised from hot alcohol; m. p. 185°. It is soluble in cold ditute alkali from which it is precipitated by acids. (Found : N, 15·30. $C_{14}H_{11}ON_3S$ requires N, 15·61 per cent.). The presence of aniline in the mother-liquor was proved.

The *disulphide* was obtained in the usual manner; m.p. 128-130°.

1-*Phenylcarbamido*-2-p-*tolyl-thiocarbamido-benzene* (XII).—An alcoholic solution of 1-*o*-aminophenyl-3-*p*-tolyl-thiocarbamide (5 g.) and phenyl *iso*cyanate (2·7g.) was heated for about 30 minutes when a white solid separated out which crystallised from alcohol; m. p. 165°. (Found: N, 14·69. $C_{21}H_{20}ON_4S$ requires N, 14·97 per cent.).

1-p-*Tolyl*-2-*keto*-4 :5-*benzo*-7-*thioketo*-1:3:6-*heptatriazine* (XXVIII).—The method of preparation was the same as in the case of the compound (XXVII). It was crystallised from hot alcohol; m.p. 175-176°. It is soluble in cold alkali from which it is precipitated by acids. (Found: N, 14·67. $C_{15}H_{13}ON_3S$ requires N, 14·79 per cent.).

The *disulphide* was obtained in the usual manner; m. p. 164°.

1-*Phenylcarbamido*-2-*methylthiocarbomido-benzene* (XIII).—An alcoholic solution of 1-*o*-aminophenyl-3-methyl thiocarbamide (3 g.) and phenyl*isocyanate* (2·4 g.) was heated for about half an hour when awhite solid separated out which crystallised from alcohol; m. p. 98°. (Found: N, 18·38. $C_{15}H_{16}ON_4S$ requires N, 18·67 per cent.).

1-Phenylamino-3:4-benzo-6-methylamino-2:5:7-thioheptadiazine (XXIX).—Two gms. of the compound (XIII) were heated under reflux with strong hydrochloric acid (60 c.c.) for about 2 hours. The clear solution, on cooling, gave out a colourless crystalline mass which again crystallised from alcohol; m. p. 195°. It is soluble in hydrochloric acid but insoluble in alkali. (Found: N, 18·78. $C_{15}H_{14}N_4S$ requires N, 19·14 per cent.).

1-Phenylcarbamido-2-allyl-thiocarbamido-benzene (XIV).—The method of preparation was the same as in the case of the compound (XIII). It was crystallised from alcohol; m. p. 160°. (Found: N, 17·41. $C_{17}H_{18}ON_4S$ requires N, 17·17 per cent.).

1-Phenylamino-3:4-benzo-6-keto-2:5:7-thioheptadiazine (XXX).—Two gms. of the compound (XIV) were heated with strong hydrochloric acid under reflux for about 2 hours. The clear solution, on cooling, gave out a crystalline mass which again crystallised from hot water acidulated with a few drops of hydrochloric acid. It is soluble in hydrochloric acid but insoluble in alkali. (Found: N, 12·46; S, 9·05. $C_{14}H_{11}ON_3S$, $3H_2O$ requires N, 12·39; S, 9·4 per cent.).

2:7-Diketo-4:5-benzo-1:3:6-heptatriazine (XXXI).—o-Phenylenediurea (XV) (prepared according to the method given in *Ber.*, 1883, **16**, 592) (2 g.) was heated under reflux with strong hydrochloric acid for about 40 minutes when a greenish black solution was obtained. The solution, on cooling, deposited crystals which were recrystallised from hot water acidulated with a few drops of hydrochloric acid. It did not melt even at 300° and sublimed slowly above 300° into shining mica-like plates. It is soluble in cold alkali from which it is precipitated by acids. (Found: N, 19·90. $C_8H_7N_3O_2$, $2H_2O$ requires N, 19·71 per cent.).

The *acetyl* derivative was crystallised from acetic acid; m.p. 190°.

o-Phenylene-sym.-diphenylcarbamide (XVI).—Phenyl *iso*cyanate (2·3 g.) was added to an alcoholic solution of *o*-phenylene-diamine (1 g.) and the solution boiled for sometime when a colourless crystalline mass came out which crystallised from alcohol; m. p. 220°. (Found: N, 15·99. $C_{20}H_{18}O_2N_4$ requires N, 16·18 per cent.).

Action of strong hydrochloric acid upon (XVI) produced no change.

Action of strong hydrochloric acid upon (XXXII): *Formation of o-Phenylene-thiourea.*—1-*o*-Aminophenyl-3-phenyl-thiocarbamide, prepared according to the method of Lellmann (*Annalen*, 1885, **228**,

212) was heated with strong hydrochloric acid under reflux for about 10 minutes when a clear solution was obtained. The solution was further boiled for about 40 minutes when greenish white crystals came out, which crystallised from hot water acidulated with a few drops of hydrochloric acid; m.p. 301-302°. Lellmann (*Annalen*, 1884, **221**, 14) gave 290° as the m.p. of this compound. (Found: N, 18·42. $C_7H_6N_2S$ requires N, 18·66 per cent.). The presence of aniline in the acid filtrate was proved.

The *disulphide* prepared in the usual manner melted at 230°.

The *acetyl* derivative melted at 200°.

1-o-*Aminophenyl*-3-o-*tolyl-thiocarbamide* (XXXIII).—It was prepared exactly in the same manner as the phenyl compound. It was crystallised from benzene; m.p. 160°. (Found: N, 16·18. $C_{14}H_{15}N_3S$ requires N, 16·34 per cent.). Like the corresponding phenyl-compound (XXXII), it gave *o*-phenylene-thiourea by the action of strong hydrochloric acid.

1-o-*Aminophenyl*-3-p-*tolyl-thiocarbamide* (XXXIV).—It was also prepared in the same manner as the corresponding phenyl compound (XXXII). It was crystallised from benzene in shining white crystals, m.p. 146-147°. (Found: N, 16·14. $C_{14}H_{15}N_3S$ requires N, 16·34 per cent.). It also gave *o*-phenylene-thiourea with strong hydrochloric acid.

1-o-*Aminophenyl*-3-*methyl thiocarbamide* (XXXV).—It was prepared exactly in the same manner as the phenyl and tolyl compounds. It was crystallised from benzene; m.p. 117°. (Found: N, 23·07. $C_8H_{11}N_3S$ requires N, 23·20 per cent.). It also gave *o*-phenylene-thiourea (m.p. 301-302°) with strong hydrochloric acid.

1-o-*Aminophenyl*-3-*allyl-thiocarbamide* (XXXVI).—It was also prepared similarly as the phenyl and tolyl compounds and was crystallised from benzene; m.p. 115°. (Found: N, 20·04. $C_{10}H_{13}N_3S$ requires N, 20·28 per cent.).

Action of strong hydrochloric acid upon (XXXVI): *Formation of* 5-*Allylamino*-2:3-*benzo*-1:4-*thiazole* (XXXVII)—The compound (XXXVI) (1·5 g.) was heated under reflux with strong hydrochloric acid (55 c.c.) for about an hour when a clear solution was obtained, which, on cooling, and dilution with water, gave no precipitate. The clear solution was next neutralised with dilute caustic soda solution under cooling when a white shining crystalline mass came out which was further crystallised from alcohol; m.p. 180°. (Found: S, 16·52. $C_{10}H_{10}N_2S$ requires S, 16·84 per cent.).

The *acetyl* derivative melted at 198°.

Action of ferric chloride upon (XXXII): *Formation of 6-Phenylamino-3:4-benzo-1:2:5-thiodiazine* (XXXVIII).—Excess of ferric chloride solution was added to 1-*o*-aminophenyl-3-phenyl-thiocarbamide (3 g.) and the mixture heated under reflux for about an hour. The reaction mixture when cooled, gave a yellow solid mass mixed with some black tarry matter. After the removal of the tarry matter with steam the residual solid was crystallised from alcohol in yellow slender needles: m.p. 155-156°. It is insoluble in alkali but soluble in hot hydrochloric acid. (Found: S, 13·13. $C_{13}H_{11}N_3S$ requires S, 13·27 per cent.).

6-p-*Tolylamino-3:4-benzo-1:2:5-thiodiazine* (XXXIX).—The method of preparation was the same as in the case of the previous compound (XXXVIII). It was crystallised from alcohol; m.p. 95°. (Found: S, 12·13. $C_{14}H_{13}N_3S$ requires S, 12·54 per cent.).

1-o-*Nitrobenzalanilido-3-phenyl-thiocarbamide* (XL).—An alcoholic solution of 1-*o*-aminophenyl-3-phenyl-thiocarbamide (2·5 g.) and *o*-nitrobenzaldehyde (1·5 g.) was heated on a water-bath under reflux for half an hour. On cooling, orange-coloured crystals gradually came out of the solution which were filtered off and crystallised from alcohol, m.p. 215°. (Found: N, 15·17. $C_{20}H_{16}O_2N_4S$ requires N, 14·89 per cent.).

1-m-*Nitrobenzalanilido-3-phenyl-thiocarbamide* (XLI).—To a hot alcoholic solution of 1-*o*-amino-phenyl-3-phenyl-thiocarbamide (2·5 g) an alcoholic solution of *m*-nitro-benzaldehyde (1·5 g.) was added when at once a yellowish white crystalline mass came out which crystallised from alcohol, m.p. 153-154°. (Found: N, 15·21. $C_{20}H_{16}O_2N_4S$ requires N, 14·89 per cent.).

1-o-*Hydroxy-benzalanilino-3-phenyl-thiocarbamide* (XLII).—It was prepared similarly as the foregoing compound and was crystallised from alcohol; m.p. 180°. (Found: N, 12·05. $C_{20}H_{17}ON_3S$ requires N, 12·10 per cent.).

1-*Benzalamino-3-phenyl-thiocarbamide* (XLIII).—Was prepared similarly as the compound (XLI); m.p. 265-267°. (Found: N, 12·92. $C_{20}H_{17}N_3S$ requires N, 12·68 per cent.).

Action of ferric chloride upon (XLIII): *Formation of 2-Phenyl-4:5-benzo-7-phenylamino-1:3:6-thiohaptadiazine* (XLIV).—1-Benzalanilino-3-phenyl-thiocarbamide (1·5 g.) was heated under reflux with an excess of ferric chloride solution for an hour when a yellow solid mixed with some tarry matter was obtained. After removing the

tarry matter with steam, the solid was crystallised from alcohol, m.p. 105°. It is insoluble in alkali but soluble in hot acids. (Found: N, 12·58. $C_{20}H_{15}N_3S$ requires N, 12·76 per cent.).

Phenyl-thio-carbamido-phenylurethane, $EtO_2C{\cdot}NH{\cdot}C_6H_4NH{-}CS{-}NHPh$.

—To a hot benzene solution of 1-*o*-aminophenyl-3-phenyl-thiocarbamide (2·4 g.) chlorcarbonic ester (1·1 g.) was added. The reaction took place at once and the separated white solid crystallised from alcohol; m.p. 288-290°. (Found: N, 13·13. $C_{16}H_{17}O_2N_3S$ requires N, 13·33 per cent.).

Action of strong hydrochloric acid upon the above compound produced no change.

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The Influence of the Variation of Intensity on the Velocity of the Decomposition of Ferric Thiocyanate and the Bleaching of Neocyanin and some other Photochemical Reactions.

By A. K. Bhattacharya and N. R. Dhar.

We have studied the influence of the variation of light intensity on several photochemical reactions and we have observed that in the majority of these reactions the velocities are more or less proportional to the square root of the intensity of incident radiation (*Cf. J. Phys. Chem.*, 1928, **32**, 1308; *Zeit. Elektrochem.*, 1926, **32**, 501; *Zeit. anorg. Chem.*, 1928, **169**, 381).

In this paper we are presenting the results obtained on the velocity of the following reactions by the change of intensity of the incident radiation from a 1000 watt gas filled tungsten filament lamp operated at 4·6 amperes:—

(1) Decomposition of an aqueous solution of ferric thiocyanate; (2) bleaching of neocyanin (Kodak) by air; reactions between (3) sodium lactate and iodine, (4) sodium tartrate and iodine, (5) chromic acid and citric acid, (6) chromic acid and tartaric acid, (7) chromic acid and lactic acid.

By changing the diameter of the aperture of an Iris diaphragm the amount of total light falling on the reacting vessel and hence the intensity was varied.

In all the reactions the thermal reaction velocities were deducted from the total change observed in light in order to get the velocity in light alone.

The changes in the concentrations of the reacting substances were determined either by suitable titrations or spectro-photometric measurements.

The diameters of the apertures of the Iris diaphragm used were 2 cm. 0·8 cm., and 0·4 cm. The intensity of light was taken to be directly proportional to the area of the aperture through which the light passed before falling on the reaction vessel.

(*i*) Diameter of the aperture = 2 cms. Area of the aperture = 3·14 sq. cm.

(*ii*) Diameter of the aperture = 0·8 cm. Area of the aperture = 0·5024 sq. cm.

(*iii*) Diameter of the aperture = 0·4 cm. Area of the aperture = 0·1256 sq. cm.

Distance of the reaction vessel from the source of light = 70 cms. The experimental results obtained are as follows.

1. *Decomposition of an aqueous solution of ferric thiocyanate* (N/250 $FeCl_3$ + N/50 NH_4CNS, 10 c.c. *each*).

Source of light:—1000 watt gas-filled tungsten filament lamp.

Temperature = 30°.

Dark:—No appreciable reaction velocity is observed.

Diameter of the aperture.	2 cm.	0·8 cm.	0·4 cm.
k_1 (Monomolecular.)	0·00175	0·000710	0·000352

Ratio of velocities.	If directly proportional to the change in intensity.	If proportional to the square root of the change in intensity.
$\frac{\text{Vel. I}}{\text{Vel. II}} = \frac{0·00175}{0·00071} = 2·46$	$\frac{3·14}{0·5024} = 6·25$	2·5
$\frac{\text{Vel. II}}{\text{Vel. III}} = \frac{0·000710}{0·000352} = 2$	$\frac{0·5024}{0·1256} = 4$	2
$\frac{\text{Vel. I}}{\text{Vel. III}} = \frac{0·00175}{0·000352} = 4·97$	$\frac{3·14}{0·1256} = 25$	5

Hence the decomposition of ferric thiocyanate is proportional to the square root of the change in intensity.

2. *Bleaching of Neocyanine* (M/7176) *by air.*

Source of light:—1000 watt gas filled tungsten filament lamp.

Temperature=30°. *Dark*:—Reaction is negligible.

Diameter of the aperture.	2 cm.	0·8 cm.	0·4 cm.
k_1 (Monomolecular.)	0·00171	0·000715	0·000366

Ratio of velocities.	If directly proportional to the change in intensity.	If proportional to the square-root of the change in intensity.
$\frac{\text{Vel. I}}{\text{Vel. II}} = \frac{0·00171}{0·000715} = 2·39$	$\frac{3·14}{0·5024} = 6·25$	2·5
$\frac{\text{Vel. II}}{\text{Vel. III}} = \frac{0·000715}{0·000366} = 1·95$	$\frac{0·5024}{0·1256} = 4$	2
$\frac{\text{Vel. I}}{\text{Vel. III}} = \frac{0\ 00171}{0·000366} = 4·7$	$\frac{3·14}{0·1256} = 25$	5

Hence the bleaching of neocyanin by air is proportional to the square-root of the change in intensity.

3. N/4·69 *Sodium lactate and* N/100 *Iodine in* N/34·3 KI, 10 c. c. *each.*

Source of light:—1000 watt gas-filled tungsten filament lamp.

Temperature=30°. *Dark*:—k_1=0·00179 at 30°.

Diameter of the aperture.	k_1 monomolecular.	True light reaction.
2 cm.	0·00336	0·00157
0·8 cm.	0·002085	0·000295
0·4 cm.	0·00186	0·00007

Ratio of velocities.	If directly proportional to the change in intensity.	If proportional to the square root of the change in intensity.
$\frac{\text{Vel. I}}{\text{Vel. II}} = \frac{0·00157}{0·000295} = 5·32$	$\frac{3·14}{0·5024} = 6·25$	2·5
$\frac{\text{Vel. II}}{\text{Vel. III}} = \frac{0·000295}{0·00007} = 4·21$	$\frac{0·5024}{0·1256} = 4$	2
$\frac{\text{Vel. I}}{\text{Vel. III}} = \frac{0·00157}{0·00007} = 22·43$	$\frac{3·14}{0·1256} = 25$	5

Hence the reaction between sodium lactate and iodine is directly proportional to the change in intensity.

4. N/2·42 *Sodium tartrate and* N/100 *Iodine in* N/34·3 KI, 10 c. c. *each.*

Source of light :—1000 watt gas filled tuingsten filament lamp.

Temperature = 30°. *Dark* :—k_1 = 0·000948.

Diameter of the aperture.	k_1 Monomolecular.	True light reaction.
2 cm.	0·00176	0·000812
0·8 cm.	0·00110	0·000152
0·4 cm.	0·000991	0·000043

Ratio of velocities.	If directly proportional to the change in intensity.	If proportional to the square root of the change in intensity.
$\frac{\text{Vel. I}}{\text{Vel. II}} = \frac{0·000812}{0·000152} = 5·34$	$\frac{3·14}{0·5024} = 6·25$	2·5
$\frac{\text{Vel. II}}{\text{Vel. III}} = \frac{0·0\ 0152}{0·000043} = 3·53$	$\frac{0·5024}{0·1256} = 4$	2
$\frac{\text{Vel. I}}{\text{Vel. III}} = \frac{0·000812}{0·000043} = 19$	$\frac{3·14}{0·1256} = 25$	5

Hence the reaction between sodium tartrate and iodine is almost directly proportional to the change in intensity.

5. 6·75N *Citric acid and* N/44·4 *Chromic acid,* 10 c. c. *each.*

Source of light :—1000 watt gas-filled tun_sten filament lamp.

Temperature = 24°. *Dark* :—k_1 = 0·000359.

Diameter of the aperature.	k_1 Monomolecular.	True light reaction.
2 cm.	0·00 781	0·000422
0·8 cm.	0·000533	0·000174
0·4 cm.	0·000453	0·000094

Ratio of velocities.	If directly proportional to the change in intensity.	If proportional to the square root of the change in intensity.
$\frac{\text{Vel. I}}{\text{Vel. II}} = \frac{0{\cdot}000422}{0{\cdot}000174} = 2{\cdot}43$	$\frac{3{\cdot}14}{0{\cdot}5024} = 6{\cdot}25$	2·5
$\frac{\text{Vel. II}}{\text{Vel. III}} = \frac{0{\cdot}000174}{0{\cdot}000094} = 1{\cdot}9$	$\frac{0{\cdot}5024}{0{\cdot}1256} = 4$	2
$\frac{\text{Vel. I}}{\text{Vel. III}} = \frac{0{\cdot}000422}{0{\cdot}000094} = 4{\cdot}5$	$\frac{3{\cdot}14}{0{\cdot}1256} = 25$	5

Hence the reaction between citric acid and chromic acid is proportional to the square root of the change in intensity.

6. N/4·27 *Tartaric acid and* N/44·4 *Chromic acid*, 10 c. c. *each*.

Source of light:—1000 watt gas filled tungsten filament lamp.

Temperature = 32°. *Dark*:—$k_1 = 0{\cdot}00305$.

Diameter of the aperature.	k_1 Monomolecular.	True light. reaction.
2 cm.	0·00705	0·00400
0·8 cm.	0·00467	0·00162
0·4 cm.	0·00385	0·00080

Ratio of velocities.	If directly proportional to the change in intensity.	If proportional to the square root of the change in intensity.
$\frac{\text{Vel. I}}{\text{Vel. II}} = \frac{0{\cdot}0040}{0{\cdot}00162} = 2{\cdot}46$	$\frac{3{\cdot}14}{0{\cdot}5024} = 6{\cdot}25$	2·5
$\frac{\text{Vel. II}}{\text{Vel. III}} = \frac{0{\cdot}00162}{0{\cdot}00080} = 2{\cdot}0$	$\frac{0{\cdot}5024}{0{\cdot}1256} = 4$	2
$\frac{\text{Vel. I}}{\text{Vel. III}} = \frac{0{\cdot}0040}{0{\cdot}00080} = 5$	$\frac{3{\cdot}14}{0{\cdot}1256} =$	5

Hence the reaction between tartaric acid and chromic acid is proportional to the square root of the change in intensity.

7. N/4·72 *Lactic acid and* N/44·4 *Chromic acid*, 10 *c.c. each.*

Source of light:—1000 watt gas filled tungsten filament lamp.

Temperature = 32°. *Dark*:—$k_1 = 0{\cdot}00195$.

Diameter of the aperture.	k_1 Monomolecular.	True light reaction.
2 cm.	0·00358	0·00163
0·8 cm.	0·00222	0·00027
0·4 cm.	0·00202	0·00007

Ratio of velocities.	If directly proportional to the change in intensity.	If proportional to the square root of the change in intensity.
$\frac{\text{Vel. I}}{\text{Vel. II}} = \frac{0{\cdot}00163}{0{\cdot}00027} = 6$	$\frac{3{\cdot}14}{0{\cdot}5024} = 6{\cdot}25$	2·5
$\frac{\text{Vel. II}}{\text{Vel. III}} = \frac{0\,00027}{0{\cdot}00007} = 3{\cdot}85$	$\frac{0{\cdot}5024}{0{\cdot}1256} = 4$	2
$\frac{\text{Vel. I}}{\text{Vel. III}} = \frac{0{\cdot}00163}{0{\cdot}00007} = 23{\cdot}3$	$\frac{3{\cdot}14}{0{\cdot}1256} = 25$	5

Hence the reaction between lactic acid and chromic acid is directly proportional to the change in intensity.

Discussion.

The experimental results show that the decomposition of ferric thiocyanate, the bleaching of neocyanin, the reactions between critic acid and chromic acid, and tartaric acid and chromic acid are practically proportional to the square root of the intensity of the incident radiation. On the other hand, the reactions between sodium lactate and iodine, sodium tartrate and iodine and chromic acid and lactic acid are practically directly proportional to the change in the intensity of the incident radiation. In presence of sunlight the reactions between chromic acid and the organic acids follow the same relations as in the case of light from the tungsten filament lamp.

The velocity measurements show that the first group of reactions is largely accelerated by light. The reactions between chromic acid and tartaric acid, and chromic acid and critic acid have been found to be more accelerated by light than the reaction between chromic acid and lactic acid. In other words, the thermal reactions are slow in comparison with the reactions in light only. In these reactions many molecules are readily activated by the absorption of radiation on illumination and consequently further increase in light intensity is not likely to increase the velocity of reaction markedly, because the number of inactive molecules available for further activation is small. Consequently those reactions, which are highly photochemical in nature, have much less chance of showing direct proportionality between the incident light and the velocity of reactions. On the other hand, the second group of reactions are only feebly accelerated by light and in this group the number of inactive molecules which are capable of being activated on increased illumination are much larger than in the first group of reactions. Consequently the velocity of these reactions will increase proportionately as the intensity of the incident radiation is increased. These relations would be observed when the incident radiation is appreciably absorbed by the reacting system. If the reacting system markedly absorb the incident radiation, direct proportionality or even square of the intensity may be expected because a marked increase in intensity and hence amount of light will lead to an increased velocity of the reaction, but if we are considering a reaction which is fast in the dark or is largely accelerated by light increased absorption of light cannot cause a concomitant increase in the velocity of the reaction because the number of molecules available for activation due to absorption of light is small. Hence, even in those reactions where the incident radiation is markedly absorbed but are largely activated by light and are highly photosensitive, instead of direct proportionality, square root relation is obtained. We find that these considerations can satisfactorily explain our experimental results obtained with about 30 reactions investigated in these laboratories.

The reaction between potassium oxalate and iodine is proportional to the square root of the incident radiation, whereas the reaction between sodium lactate and iodine is directly proportional to the intensity. If we assume that in presence of light a molecule of iodine is atomised, we can explain the intensity effect on the

reaction between potassium oxalate and iodine but this conception that the halogen molecules are atomised on illumination does not help us in understanding the mechanism of those photochemical reactions with halogens as one of the reacting substances and where the velocity of reaction is directly proportional to the intensity of incident light. Our experimental results show that the reaction between sodium lactate and iodine is only slightly accelerated by light and consequently the inactive molecules available for activation on illumination is large and consequently a direct proportionality is observed. We are of the opinion that this explanation of the difference of intensity effect on different reactions is more satisfactory than any of the existing views.

In numerous pu blications from these laboratories we have shown that the temperature coefficient of a photochemical reaction is smaller than the temperature coefficient of the reaction in the dark, and the greater the acceleration produced by light, the less the lowering of the temperature coefficient; consequently, in those reactions where the velocity is directly proportional to the intensity of incident radiation, the lowering of temperature coefficient due to light will be less than in those reactions where the velocities are more or less proportional to the square root of the intensity of incident radiation. Hence we are in a position to predict the intensity effect on a photochemical reaction by measurement of its speed and temperature coefficient in light and in the dark.

Summary.

1. The influence of the variation of the intensity of the radiation from a 1000 watt gas filled tungsten filment lamp was investigated on seven photochemical reactions.

2. The experiments show that the velocities of the following reactions are proportional to the square root of the incident radiation:—(*a*) Decomposition of ferric thiocyanate; (*b*) bleaching of neocyanin; (*c*) reactions between citric acid and chromic acid, and (*d*) tartaric acid and chromic acid.

The velocities of the following reactions are directly proportional to the intensity of the radiation:—

(*a*) Sodium lactate and iodine; (*b*) sodium tartrate and iodine; (*c*) lactic acid and chromic acid.

3. The two important factors, which are of consequence in the relation between intensity and the velocity of a reaction, are:—(1) amount of absorption of the incident radiation by the reacting system, and (2) the acceleration of the reaction in presence of light. When the absorption of radiation is high and the reaction is not markedly photochemical in nature and the velocity of the reaction in the dark is appreciable, direct proportionality or even square of intensity is likely to be observed. On the other hand, when the reaction is highly photochemical in nature and the velocity of the dark reaction is practically negligible, square root relation will be expected.

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Experiments on the Synthesis of ψ-Opianic Acid. Part I.

By Satyendra Nath Chakravarti.

ψ-Opianic acid (IV) was first obtained by Perkin by the hydrolysis of berberal by means of dilute sulphuric acid (Perkin, *J. Chem. Soc.*, 1890, **57**, 1064). Its importance is apparent when it is remembered that the constitution assigned to berberal and berberine by Perkin and Robinson (*J. Chem. Soc.*, 1910, **97**, 319) is based in the first instance on that of ψ-opianic acid.

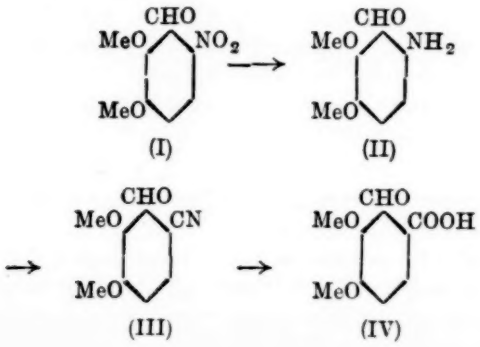
The first attempt to synthesise ψ-opianic acid was made by Solomon by the oxidation of ψ-meconine (*Ber.*, 1887, **20**, 888) when he discovered the striking fact that whilst meconine was oxidized quantitatively to opianic acid, ψ-meconine was unaffected under similar conditions.

The next important attempt on record is that of Perkin and Stoyle, (*J. Chem. Soc.*, 1923, **123**, 3173) when they tried to obtain ψ-opianic acid from *iso*vanillic acid by an application of the Tiemann-Reimer reaction.

It was found however that the only product obtained by the action of chloroform and caustic potash was 5-hydroxy-4-methoxy-2-aldehydo-benzoic acid.

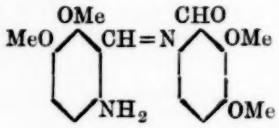
The last attempt on record was made by Edwards, Perkin and Stoyle (*J. Chem. Soc.*, 1925, **127**, 196) when they tried to obtain it by the oxidation of ψ-meconine on lines similar to those of Solomon.

The first scheme that has now been tried will be clear from the following formulæ-sketch:



6-Nitro-2: 3-dimethoxy-benzaldehyde (I) was obtained by the separation of the nitration product obtained by the nitration of *o*-veratraldehyde (Perkin, Roberts, and Robinson, *J. Chem. Soc.*, 1914, **105**, 2389; Perkin, Robinson, and Stoyle, *J. Chem. Soc.*, 1924, **125**, 2355). During the course of these experiments, the interesting observation was made that, contrary to the statements of the previous investigators, the nitration product was obviously a mixture and that it could be separated by a very careful series of fractional crystallisations, into the two components, 6-nitro-2: 3-dimethoxy-benzaldehyde and 5-nitro-2: 3-dimethoxy-benzaldehyde.

As a result of a number of comparative experiments, it was found that the reduction of 6-nitro-2: 3-dimethoxybenzaldehyde to the corresponding amino compound (II) is best effected by means of ferrous sulphate and ammonia under the conditions described. The hydrochloride, the phenylhydrazone and the benzoyl derivative of the 6-amino-2: 3-dimethoxy-benzaldehyde (II), have been prepared. The amino compound (II) itself is very unstable and on boiling with solvents like alcohol passes into a curious condensation product, which is a yellow crystalline base, m.p. 235° and may have the following constitution (V).



(V)

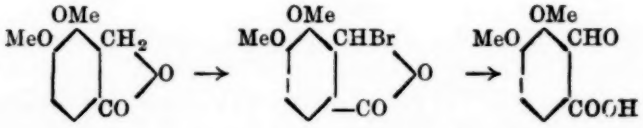
The next step in the synthesis consisted in the displacement of the amino group by the nitrile group by an application of the usual Sandmeyer's reaction. Though a large number of experiments were tried, the conversion of 6-amino-2: 3-dimethoxy benzaldehyde (II) into 6-cyan-2: 3-dimethoxy benzaldehyde could not be effected and therefore this simple route to the synthesis of ψ-opianic acid had to be abandoned. In this connection it is interesting to observe that there does not seem to be on record the synthesis of a single *o*-cyan-aldehyde of the aromatic series. An attempt by Rilliet and Kreitman to prepare 6-cyan-piperonal from 6-amino-piperonal was unsuccessful (*Helv. Chim. Acta*, 1921, **4**, 596).

The second series of attempts centred on the oxidation of ψ-meconine. It seemed curious that it should be found impossible to oxidize an alcohol to the aldehyde, and therefore the problem of

oxidation of ψ-meconine and salts of ψ-meconinic acid was reinvestigated. For the oxidation the action of the following oxidizing agents was investigated under a variety of different conditions: (*i*) manganese dioxide and dilute sulphuric acid ; (*ii*) dichromate and sulphuric acid ; (*iii*) lead dioxide and dilute sulphuric acid ; (*iv*) alkaline hydrogen peroxide ; (*v*) potassium permanganate in acetone solution; (*vi*) alkaline permanganate. Unfortunately, however, ψ-meconine is so resistant to oxidation that no trace of the aldehydo-acid could be isolated, the ψ-meconine being either recovered unchanged, or in extreme cases completely destroyed.

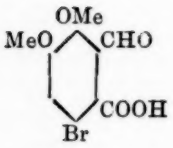
In view of the failure of the attempts at direct oxidation not only of ψ-meconine, but also of 3 : 4-methylene-dioxy-phthalide (Perkin and Trikojus, *J. Chem. Soc.*, 1926, **129**, 2931) and of 4 : 5-methylene-dioxy-phthalide (Stevens and Robertson, *J. Chem. Soc.*, 1927, **131**, 2791) to aldehydo-acids it was thought desirable to devise methods by which the conversion of the phthalide to aldehydo-acid could be easily accomplished. The next two schemes for the synthesis of ψ-opianic acid were developed with this idea in view

The first of these devices would be clear from the following scheme :—



The idea was to introduce a halogen atom in the side chain of the phthalide and then to hydrolyse the product to the corresponding aldehydo-acid. In the case of ordinary phthalide the introduction of a halogen atom in the side chain can be readily effected (Racine, *Annalen*, 1887, **239**, 79; Gabriel, *Ber.*, 1916, **49**, 1912) and the halogenated product is smoothly hydrolysed to *o*-phthalaldehydic acid.

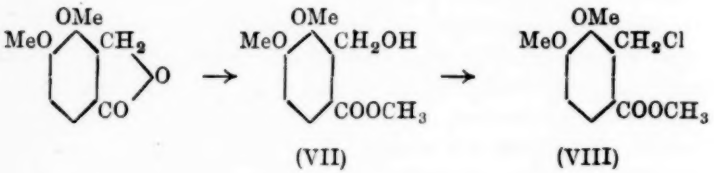
Bromination of ψ-meconine was tried at temperatures varying from 140° to 180° in bright sunlight. Unfortunately in every case, as it was feared at the outset, part of the bromine enters the nucleus and part of it goes to the side chain. The hydrolysed product consists mainly of an aldehydo-acid containing bromine in the nucleus, which probably has the constitution (VI). This substance



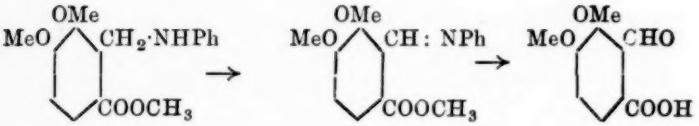
(VI)

has not yet been obtained in a pure form. Experiments are in progress for preparing its derivatives.

The next scheme that was attempted would be clear from the following formulae—

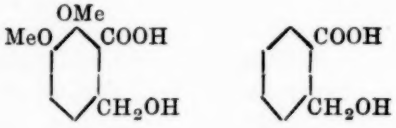


(VII) (VIII)



(IX) (X) (XI)

The first stage in the scheme consisted in converting ψ-meconine into ψ-meconinic ester. It is well known that the acids of the type of meconinic acid (XII) and 2-hydroxymethylbenzoic acid (XIII) are very unstable and not a single ester of this class of acids has so far been prepared. It was surprising therefore to find that ψ-meconinic

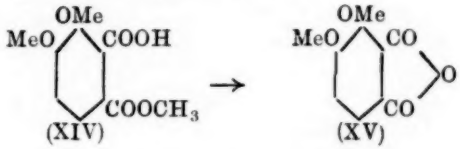


(XII) (XIII)

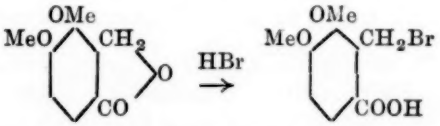
ester could be readily prepared from ψ-meconine by converting the latter into silver ψ-meconinate through the barium salt and finally treating the silver salt with methyl iodide in presence of ether. ψ-Meconinic ester is a beautifully crystalline substance, m.p. 72—3°.

The next step consisted in converting ψ-meconinic methyl ester (VII) into methyl 2-chlormethyl-3:4-dimethoxy-benzoate (VIII), but

inspite of a large number of attempts with reagents like thionyl chloride, phosphorous pentachloride, hydrochloric acid gas and hydrobromic acid, the replacement of the hydroxyl by a halogen atom could not be effected, the unstable ester being readily decomposed by these reagents back into ψ-meconine. In this connection it is of interest to note that in a somewhat similar case Wegscheider and Rusnov (*Monatsh.*, 1903, **24**, 385; *Sitzungsber.*, 1903, **112**, 217) found it impossibis to convert hemipinic acid-methyl ester (XIV) into the corresponding acid chloride, hemipinic anhydride (XV) being the main product of reaction.



Attempts were next made to prepare 2-chlor- or brom-methyl-3 :4-dimethoxybenzoic acid (XVI) from ψ-meconine by the action of phosphorous pentachloride or hydrobromic acid. In the course of these experiments it was found that ψ-meconine was unaffected by



(XVI)

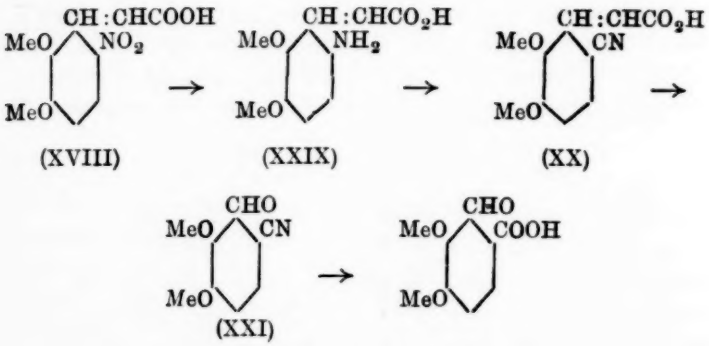
phosphorous pentachloride at ordinary temperature or by a short treatment at 100° or even at 160°, and it was left uuchanged by hydrobromic acid in glacial acetic acid under conditions under which the lactone of 6-hydroxy-methyl-homopiperonylic acid is converted into 6-brom-methyl homopiperonylic acid (Stevens, *J. Chem Soc.*, 1927, **131**, 186). This remarkable stability of ψ-meconine is hard to understand and further experiments on the action of hydrobromic acid on ψ-meconine are in progress.

The fifth scheme for the synthesis of ψ-opianic acid consisted in attempts at conversion of 2-cyan-veratric acid (XVII) into ψ-opianic acid by means of stannous chloride in presence of an

ethereal solution of hydrogen chloride according to the vauable method for the conversion of nitriles into aldehydes devised by Stephen (*J. Chem. Soc.*, 1925, **127**, 1874).

2-Cyan-veratric acid which had first been obtained by Hoogeworff and Van Dorp (*Rec. trav. chim.*, 1895, **14**, 272) from hemipinic acid has now been prepared from 2-amino-veratric acid by an application of the Sandmeyer's reaction, 2-aminoveratric acid itself being obtained from vanillin by a modification of the methods of Pschorr and Sumuleneau (*Ber.*, 1899, **32**, 3408). The attempts to reduce 2-cyan-veratric acid (XVII) to ψ-opianic acid by Stephen's method were unsuccessful, undoubtedly largely due to steric factors as both the *ortho*-positions to the nitrile group are substituted. Attempts to reduce the ester of (XVII) were also unsuccessful

The sixth and the final scheme that was tried would be clear from the following formulae sketch:—

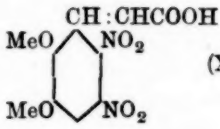


(XVIII) (XXIX) (XX) (XXI)

The easiest way to make 6-nitro-2:3-dimethoxy-cinnamic acid (XVIII), the essential starting substance for this scheme, it would appear was to condense 6-nitro-2:3-dimethoxy-benzaldehyde with malonic acid in pyridine solution in presence of piperidine. Contrary to usual experience, it was found that by this method only a 10 % yield of 6-nitro-2:3-dimethoxy-cinnamic acid is obtained, and as the starting substance was difficult to obtain in large quantities, this method of preparation had to be abandoned. Ultimately it was found that a better method for making this acid was by the nitration of 2 : 3-dimethoxy-cinnamic acid. The nitration of 2 : 3-dimethoxy-cinnamic acid was first carried out by Rubenstein (*J. Chem. Soc.*, 1926, **129**, 648) who, without any adequate proof, assumed that the nitration product consisted of a mixture of

5-nitro-2 : 3-dimethoxy-cinnamic acid and 6-nitro-2 : 3-dimethoxy cinnamic acid, the former preponderating. As the condition of nitration was also not definitely stated, the whole problem of nitration was reinvestigated. Nitration was carried out under a variety of different conditions with a view to obtain maximum yield of 6-nitro-2 : 3-dimethoxy-cinnamic acid.

In the nitration of ordinary cinnamic acid the yield of the *ortho*-nitro-cinnamic acid increases with the increase in concentration of nitric acid (Muller, *Annalen*, 1882, **212**, 128). It was therefore thought that if fuming nitric acid were used in place of ordinary nitric acid for nitration, the yield of the 6-nitro-2 : 3-dimethoxy-cinnamic acid might be improved. When, however, the nitration was carried out with fuming nitric acid, the product consisted mainly of a dinitro-cinnamic acid which is of interest in view of the fact that five vicinal hydrogen atoms are substituted in this compound. The dinitro-compound is probably 5 : 6-dinitro-2 : 3-dimethoxy-cinnamic acid (XXII).



(XXII)

The conditions which were ultimately chosen for nitration is described (p. 223). Even under these conditions the nitration product consists of only about 10 % of 6-nitro-2 : 3-dimethoxy-cinnamic acid (XVIII), while the rest consisted of 5-nitro-2 : 3-dimethoxy-cinnamic acid. The separation of the two nitro-compounds as described by Rubenstein (*loc. cit.*) was found to be tedious, and later on it was found that the two acids could be more readily separated if the nitration product was converted straightway into a mixture of methyl esters and the esters were then separated by a careful series of fractional crystallisation from alcohol and benzene.

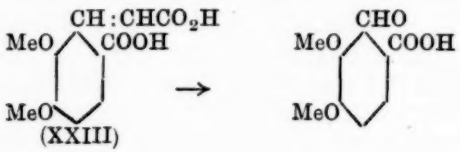
6-Nitro 2 : 3-dimethoxy-cinnamic acid, m. p. 220°, and its ethyl and methyl esters are described in the experimental section (p. 225). Its constitution was proved in the first place by showing its identity with 6-nitro-2 : 3-dimethoxy-cinnamic acid obtained from 6-nitro-2 : 3-dimethoxy-benzaldehyde, whose constitution has already been established by Perkin, Robinson and Stoyle (*J. Chem. Soc.*, 1924, **125**, 2355), by means of mixed melting points of the acid and their esters. In the second place the acid, m. p. 220°,

obtained after separation was oxidized by means of alkaline permanganate in presence of benzene to 6-nitro-2:3-dimethoxy-benzaldehyde, m. p. 110°.

6-Nitro-2:3-dimethoxy-cinnamic acid is smoothly reduced to 6-amino-2 : 3-dimethoxy-cinnamic acid (XIX) by means of ferrous sulphate and ammonia. The latter acid was next converted into 6-cyan-2 : 3-dimethoxy-cinnamic acid by an application of the usual Sandmeyer's reaction.

The next step in the scheme consisted in the oxidation of 6-cyan-2 : 3-dimethoxy-cinnamic acid (XX) to 6-cyan-2 : 3-dimethoxy-benzaldehyde (XXI). It was hoped that this oxidation would be easily effected by alkaline permanganate in presence of benzene, but so far all the experiments in this direction have been unsuccessful, the only neutral oxidation product obtained consisting of a high melting substance, whose constitution so far, owing to the small amount of the substance being available, has not been completely cleared up. The failure of this oxidation is very curious for, under similar conditions, 5-cyan-2 : 3-dimethoxy-cinnamic acid gives 5-cyan-2 : 3-dimethoxybenzaldehyde in an yield of 80 % (Chakravarti and Perkin, *J. Chem., Soc.*, 1929, **135**, 195), while 6-nitro-2: 3-dimethoxy cinnamic acid gives 6-nitro-2 : 3-dimethoxy-benzaldehyde in fairly good yields (see p. 26).

It was next thought that oxidation of 6-carboxy-2 : 3-dimethoxy-cinnamic acid (XXIII) to ψ-opianic acid might, perhaps, be easier to accomplish. For this purpose 6-carboxy-2 : 3-dimethoxy cinnamic acid (XXIII) was prepared by the hydrolysis of 6-cyan-2 : 3-dimethoxy-cinnamic acid (XX) by means of 10% caustic soda solution.



But attempts at oxidation by means of alkaline permanganate under conditions similar to those by which Ehrlich obtained *o*-phthalaldehydic acid from *o*-carboxy-cinnamic acid (*Monatsh.*, 1889, **10**, 576; *Sitzungsber.*, 1889, **98**, 1594) and under other conditions were unsuccessful, an acid, m. p. 202° being obtained which differed from ψ-opianic acid in properties.

Though all the attempt to synthesise ψ-opianic acid have so far been unsuccessful, it is hoped that the synthesis of this acid would soon be accomplished in light of these fresh results.

EXPERIMENTAL.

The nitration of *o*-veratraldehyde was carried out essentially under the conditions described by Perkin, Roberts and Robinson (*J. Chem. Soc.*, 1914, **105**, 2389). The product of nitration was crystallised from methyl alcohol and then subjected to a series of careful fractional crystallisations when the heterogeneous character of the product became evident and from the more soluble fractions small quantities of 6-nitro-2:3-dimethoxybenzaldehyde, m. p. 110°, was isolated in pure condition (1 g. from 10 g.) (Found: N, 6·7. $C_9H_9O_5N$ requires N, 6·6 per cent.). Separation on a larger scale was effected under conditions similar to those described by Perkin, Robinson and Stoyle (*J. Chem. Soc.*, 1924, **125**, 2357).

For reduction of 6-nitro-2:3-dimethoxy-benzaldehyde (I) to the corresponding amino-derivative (II) the actions of the following reducing agents were investigated:—(1) ammonium sulphide on the *p*-toluidine derivative of the nitro-aldehyde; (2) sodium sulphide on the *p*-toluidine derivative under conditions similar to those recommended by Rilliet and Kreitmann (*Helv. Chim. Acta*, 1921, **4**, 591); (3) ferrous sulphate and sodium carbonate on the bisulphite compound of the nitro-aldehyde (compare Troger and Dunker, *J. pr. Chem.*, 1925, (ii), **111**, 208); (4) ferrous sulphate and ammonia on the bisulphite compound of the nitro-aldehyde; (5) ferrous sulphate and ammonia.

As a result of these comparative experiments it was found that the reduction is best effected by means of ferrous sulphate and ammonia under the following conditions:—

To a solution of ferrous sulphate (26 g. in 60 c. c. water) was added 6-nitro-2:3 dimethoxy-benzaldehyde (2 g.) and the mixture heated up to boiling and to the boiling mixture was added gradually concentrated ammonia (11 c. c.), and the whole shaken vigorously. The mixture was heated for a quarter of an hour more and filtered hot. The filtrate as well as the precipitate was thoroughly extracted with ether (ten times). The ethereal solution (A) was dried over sodium sulphate and the solution

saturated with dry hydrochloric acid gas. The *hydrochloride* of the amine was precipitated as an almost colourless powder (1·65 g.). It was filtered, washed with dry ether and dried in a desiccator. (Found: C, 49·4 ; H, 5·5. $C_9H_{11}O_3N$, HCl requires C, 49·6 ; H, 5·5 per cent).

In a previous experiment it was found that if the ethereal extract (A) of the amine as obtained above was concentrated down and the residue crystallised from benzene or alcohol, the amine first formed was changed into a complex condensation or polymerisation product. The substance thus obtained crystallised in yellow prisms, m.p. 235°, and was insoluble in dilute acids, whereas the crude amine obtained by removal of ether at ordinary temperatures under reduced pressure was readily soluble in dilute mineral acids. (Found: N, 8·28. $C_{18}H_{20}N_2O_5$ requires N, 8·14 ; the amine (II) requires N, 7·73 per cent.).

The benzoyl derivative.—Benzoyl chloride (1 c. c.) was added to an ethereal extract (A) of the amine (from 1 g. of the nitro-compound) and the whole kept overnight, the ether removed, and the residue was shaken up with dilute caustic soda. The whole was extracted with benzene, the extract dried over sodium sulphate, the solvent removed by distillation, and the residue was crystallised twice from alcohol. The benzoyl derivative of 6-amino-2:3-dimethoxy-benzaldehyde was thus obtained in beautiful needles, m. p. 150°. (Found: C, 67·1 ; H, 5·2. $C_{16}H_{15}O_4N$ requires C, 67·4 ; H, 5·3 per cent.).

The *phenylhydrazone* of 6-amino-2:3-dimethoxy-benzaldehyde was prepared by adding a slight excess phenylhydrazine (0·8 g.) to the ethereal extract (A) of the amine (from 1 g. of the nitro-compound) and allowing the whole to stand overnight, removing the ether, boiling the product for a few minutes with alcohol and finally crystallising the product from benzene. It was obtained as colourless plates, m. p. 133°.

Diazotization of the amine (II) *and attempts at replacement of the amino group by nitrile.*—(*i*) A clear diazo solution is not obtained when diazotization is carried on under usual conditions. 0·1 G. of the amine or amine hydrochloride is taken up in dilute hydrochloric acid (2 c. c.). As soon as a drop of sodium nitrite is added to this solution a red ochreous precipitate appears, which increases as more sodium nitrite is added and

the whole of the amine is precipitated as a reddish powder, insouble in water, and soluble in alcohol from which it could not be obtained crystalline. (*ii*) In concentrated hydrochloric acid diazoti zation seems to take place and a clear solution is obtained wh ich gives a red dye when coupled with β-naphthol in alkaline solution. When a clear diazotized solution was added to the required amount of hot potassium cuprous cyanide solution in the usual manner, not a trace of the cyanide could be isolated, either by steam-distillation of the product or extraction with benzene or chloroform. (*iii*) The amine hydrochloride (0·2 g.) was taken up in absolute alcohol (10 c. c.) and amyl nitrite (0·3 g.) added at 0° or at usual temperature with constant stirring till the whole went into solution. On diluting with ether, the diazo-compound separated out and was either extracted with ice-water or filtered rapidly. The solution of the diazo-compound thus obtained was treated with the required amount or excess of potassium-cuprous cyanide in the usual way, but no cyanide could be isolated. (*iv*) Attempts at diazotization in glacial acetic acid in presence of the required amount of hydrochloric acid and replacement by the nitrile group were also unsuccessful. The only products that were obtained were either tarry substances which were not hydrolysed to any acid, or substances which were insoluble in organic solvents.

Action of Alkaline Hydrogen peroxide on ψ-Meconine.—(*i*) ψ-Meconine (0·1 g.) was dissolved in 2·5 % caustic soda solution (10 c. c.) and treated with 6 % hydrogen peroxide (5 c. c.) and kept for 12 hours. No visible reaction takes places. On acidification with concentrated hydrochloric acid and allowing to stand, beautiful long needles, m.p. 123-24° separated. The precipitate was insoluble in sodium carbonate and was found to be unchanged ψ-meconine. The filtrate was extracted with ether, the solution dried and the solvent removed when very slight residue was obtained which consisted of ψ-meconine. (*ii*) ψ-Meconine (0·1 g.) was dissolved in 2·5 % caustic soda solution (10 c. c.) by warming and treated with 30 % hydrogen peroxide (1 c. c.) and kept for 12 hours. No visible reaction takes place. On acidification beautiful long needles gradually separated which proved on examination to be the unchanged ψ-meconine. The filtrate was extracted with ether, and ether removed when a slight non-acid residue was obtained. (*iii*) ψ-Meconine (0·1 g.) was dissolved in 2·5 % caustic soda solution

(10 c. c.) and treated with excess of 30 % hydrogen peroxide and the whole warmed up for about an hour. ψ-Meconine was again recovered unchanged.

Action of Potassium Dichromate and dilute Sulphuric acid on ψ-Meconine.—(*i*) To a boiling solution of ψ-meconine (0·2 g.) in water was gradually added a mixture of potassium dichromate (0·1 g.) sulphuric acid (1·5 c. c.) and water (4 c. c.) and warmed for 15 minutes. On allowing to cool, most of the ψ-meconine separated unchanged. (*ii*) A solution of potassium dichromate (0·2 g.) in a mixture of sulphuric acid (1 c. c.) and water (1·5 c. c.) was added to ψ-meconine (0·1 g.), and the whole boiled for a few minutes. Most of the ψ-meconine was recovered unchanged, while part of it was oxidized away and could not be recovered.

Action of manganese dioxide and dilute sulphuric acid on ψ-Meconine.—(*i*) ψ-Meconine (0·3 g.) was boiled under reflux with 20% sulphuric acid (5 c.c.) and finely powdered manganese dioxide (1 g.) for three hours. The resulting solution on filtration and cooling deposited beautiful needles of unchanged ψ-meconine. The mother-liquor was extracted with ether, the ether solution dried and the ether evaporated off when a slight non-acid residue was left. (*ii*) Heating was continued for six hours under the above conditions. Most of the ψ-meconine was again recovered unchanged.

Action of Lead dioxide and Sulphuric acid on ψ-Meconine.—ψ-Meconine (0·1 g.), water (1 c.c.) and lead dioxide (0·5 g.) were kept at 100° while dilute sulphuric acid was run in. The mixture was heated for an hour, and filtered, when ψ-meconine separated on cooling.

Action of Alkaline Permanganate on ψ-Meconine.—(*i*) ψ-Meconine (0·2 g.) was dissolved in 2·5% caustic soda solution (10 c.c.) by warming and to the warm solution 1% permanganate solution (11 c.c.) was gradually added and the whole kept for twenty four hours. The whole was warmed up again and filtered and the filtrate acidified. On standing beautiful needles of unchanged ψ-meconine separated. No acid could be isolated from the mother-liquors by extraction with ether etc. (*ii*) ψ-Meconine (0·1 g.) was dissolved in 2·5 % caustic soda solution (10 c.c.) and to the warm solution was gradually added 1% permanganate (20 c.c.) and the whole warmed up for an hour on the water-bath and kept for twenty four hours. On acidification nothing is precipitated, all the ψ-meconine having been oxidized

away. On extraction with ether a slight amount of an acid, m.p. 180° was obtained, which was found to be hemipinic acid, the rest of the meconine appears to have been completely destroyed. *(iii)* ψ-Meconine (0·1 g.) was dissolved in 2·5 % caustic soda (10 c.c.) and to the warm solution was gradually added 1% permanganate (10 c.c.) and the whole warmed up for an hour on the water-bath, and kept for twenty four hours, filtered and acidified. On standing part of the ψ-meconine separated out, while the mother-liquor on extraction with ether gave some hemipinic acid. Similar results were obtained when the oxidation was carried out with permanganate in acetone solution.

Bromination of ψ-Meconine.—ψ-Meconine (1·9 g.) was heated in a test tube, fitted up with a reflux-condenser and dropping funnel, to 150° in an oil-bath and dry bromine (·5 c.c.) was gradually added by means of the dropping funnel in bright sunshine in the course of half an hour. Bromination evidently takes place and hydrobromic acid gas was given off. After being allowed to stand over lime, attempts were made without success to crystallise it from the usual organic solvents. It came out as a gum from benzene etc. On trying to crystallise the product from formic acid, a small amount of a crystalline substance melting over 280° was obtained. This substance was insoluble in cold sodium carbonate, but dissolved readily in dilute caustic soda in the cold. It has not yet been found possible to get enough of this substance to characterise it by analysis. But most of the brominated product remained in formic acid solution and did not crystallise on concentration etc. Therefore the product was diluted with water and kept for a few days, when a gum separated, which on boiling with water passed into an acid crystallising in fine needles, m.p. about 200°. This acid contains bromine and forms a compound possibly, an oxime with hydroxylamine.

Some of the freshly borminated product was then examined. It was insoluble in cold sodium carbonate. *(i)* A little of the crude brominated product was boiled with 25 times its weight of water for a couple of hours and then cooled. The product thus obtained was found to be a mixture. Part of it dissolved in cold sodium carbonate while the undissolved part was found to be a mixture of the unchanged ψ-meconine and brominated product. The part soluble in cold sodium carbonate was thrown down on acidification. In the crude state it melted at about 90°, and was readily soluble in alcohol and only sparingly in water. It did not crystallise in contact with

the usual organic solvents. On boiling with much water part of it dissolved, leaving an undissolved gum. From the aqueous solution an amorphous wooly mass melting at about 200° c me down. It contains bromine. (*ii*) Hydrolysis of the crude brominated product was carried out by boiling for four hours with dilute sodium carb onate solution. Again a similar product to the above was obtaine d, part of it consisting of an amorphous acid, and part of the unchanged ψ-meconine etc. (*iii*) Bromination was next carried out at different temperatures *viz.* at 160°, 170° and 180°, but the brominated pro ducts thus obtained did not differ in fundamental characters, from brominated product obtained by the previous method.

Methyl ψ-meconinate. Silver ψ- meconinate (compare Perkin, *J. Chem. Soc.*, 1890, **57**, 1074).—ψ-Meconine (5 g.) was dissolved in barium hydroxide solution (15 g. freshly crystallised in 60 c.c. water) and in the boiling hot solution carbon dioxide was passed till the exce ss of barium hydroxide was precipitated as barium carbonate. The mix ture was then filtered, the filtrate allowed to cool and treated with ex cess of silver nitrate solution (8 g. in solution). A white curdy precipitate was thr own down. It was kept over-night, filtered, washed with water, me thyl alcohol and then ether and allowed to dry in a vacuum desiccator over sulphuric acid. The silver salt was finely powdered, covered with dry ether (150 c.c.) and gently boiled under reflux on a water-bath with excess of methyl iodide (20 c.c.) for 3 hours. After filtering from silver salts, the ethereal solution was concentrated and kept when beautiful prismatic crystals of the ester, m.p. 72°-73° separated. (Found : C, 58·6; H, 6·1. $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2 per cent.).

Attempts at replacement of the hydroxyl group in the ester by chlorine.—(*i*) Finely powdered ψ-meconinic ester (1·13 g.) was mixed with dry and pure pyridine (0·4 g.) and to the mixture was gradually added at ordinary temperature (10°), freshly distilled thionyl chloride (0·4 c.c.). Some reaction appeared to take place and ψ-meconinic ester went into solution. On allowing to stand the whole solidified. It was kept for twenty four hours in a test-tube fitted with a calcium chloride tube, the product taken up in a little cold water, filtered and then crystallised from benzene. The crystallised substance melted at 123°-124° and was identified as ψ-meconine, by the method of mixed melting points. (*ii*) ψ-Meconinic ester (0·5 g.) was dissolved in dry and redistilled chloroform and to the solution cooled

to 0° was gradually added finely pulverised phosphorous pentachloride (0·6 g.) and the whole allowed to stand for an hour at 0°. The ensuing solution was concentrated in vacuum below 100° and the residue crystallised from benzene when a substance melting at 123°-124° was obtained and was identified as ψ-meconine. (*iii*) ψ-Meconinic ester (0·2 g.) was dissolved in ether and the ether solution was saturated with dry hydrochloric acid gas in presence of sodium sulphate (fused). The whole was kept for 12 hours, filtered, and the ether solution concentrated after being thoroughly washed with water and dried. The concentrated solution deposited on standing crystals of ψ-meconine. (*iv*) ψ-Meconinic ester (0·2 g.) was treated with a large excess of hydrobromic acid dissolved in glacial acetic acid and the whole kept for 12 hours. Nothing crystallised out, so the whole was diluted with water and extracted with ether, and the ethereal solution dried and concentrated, when ψ-meconine was obtained.

Action of Phosphorous pentachloride on ψ-Meconine.—(*i*) Phosphorous pentachloride has no action on ψ-meconine at ordinary temperature or when heated on the water-bath for a short time. (*ii*) Phosphorous pentachloride and ψ-meconine were heated for an hour in an oil-bath at 160°. The product was treated with ice-water and the part insoluble in cold water crystallised from benzene, when unchanged ψ-meconine separated. In another experiment the fresh product was treated with methyl alcohol, but again ψ-meconine was obtained. (*iii*) At higher temperatures dark uncrystallisable substances were obtained.

Action of hydrobromic acid in glacial acetic acid on ψ-meconine.—ψ-Meconine dissolved in a little glacial acetic acid was treated with a large excess of hydrobromic acid in glacial acetic acid, and the whole kept overnight. No reaction appeared to take place. On dilution unchanged ψ-meconine separated. Action of hydrobromic acid at higher temperatures would be further investigated.

2-*Cyan-veratric acid* (XVII).—A mixture of 2-amino-veratric acid (7·4 g.), which was prepared by a slight modification of the methods of Pschorr and Sumuleneau (*Ber.*, 1899, **32**, 3408) and of Pisovschi (*Ber.*, 1910, **43**, 2137) from vanillin, water (50 c.c.) and concentrated hydrochloric acid (10 c.c.), was treated at 0° with sodium nitrite (2·9 g. dissolved in water) and the clear diazo solution was gradually added to a hot solution of potassium-cuprous-cyanide obtained by adding to a solution of coppersulphate

(10 g. in 60 c.c. water) a solution of potassium cyanide (11·2 g. in 20 c.c. water). After the addition of the diazo solution to the cuprous cyanide solution, the mixture was heated for ½ hour on the water-bath, cooled and made slightly acid by means of concentrated hydrochloric acid, when the cyano-acid (XVII) was precipitated. The precipitate was filtered, washed, and dissolved in cold sodium carbonate, filtered from undissolved inorganic substances and the clear solution acidified with concentrated hydrochloric acid. The cyano-acid thus precipitated was collected and crystallised from alcohol with the aid of animal charcoal. It crystallised from alcohol in beautiful long needles, m.p. 208-9.° (Found: C, 58·2 ; H, 4·5. $C_{10}H_9O_4N$ requires C, 58·0 ; H, 4·3 per cent.). 2-Cyan-veratric acid is sparingly soluble in ether or chloroform and is readily hydrolysed by boiling with dilute hydrochloric acid to hemipinic acid.

Attempts at conversion of 2-cyan-veratric acid into ψ-opianic acid.—(*i*) Anhydrous stannous chloride (3 g.), prepared from the pyridine derivative by the method recommended by Stephen (*J. Chem. Soc.*, 1925, **127**, 1874) was finely powdered, sieved, suspended in dry ether (20 c.c.) and saturated with dry hydrogen chloride until it had dissolved and the mixture had separated into two layers. 1-Cyan-veratric acid (1 g.) was then added in ether suspension with rapid shaking in a flask fitted with calcium chloride tube. After twelve hours the whole was filtered off and the precipitate heated with water for three hours. After cooling, the aqueous solution was extracted with ether, the ethereal solution concentrated and then extracted three times with sodium carbonate solution. The sodium carbonate solution was concentrated and acidified. An acid m.p. 180° was precipitated, which on recrystallisation from water was obtained in beautiful prismatic needles and was proved to be hemipinic acid. (Found: C, 52·9 ; H, 4·4. $C_{10}H_{10}O_6$ requires C, 53·1 ; H, 4·4 per cent.). The hemipinic acid was evidently formed by the hydrolysis of the unchanged 2-cyan-veratric acid. (*ii*) Finely powdered and sieved anhydrous stannous chloride (3 g.) was suspended in dry ether (20 c.c.) and dry hydrogen chloride was passed into the ether suspension, until it had dissolved and separated in two layers. 2-Cyan-veratric acid (1 g.) dissolved in absolute alcohol was then added with rapid shaking in a flask fitted with a calcium chloride tube. The whole was

allowed to stand for twenty-four hours. No deposition of a double compound took place. The upper ethereal layer on separation and evaporating down gave a substance melting at 228°, which on examination was found to be hemipinimide.

2:3-*Dimethoxy-cinnamic acid.*—This acid had previously been obtained by condensation of *o*-veratraldehyde with (*i*) acetic anhydride and sodium acetate at 200° (Heinrich and Krannichfeldt, *Ber.*, 1913, **46**, 4021), or (*ii*) with ethyl acetate in presence of sodium (Perkin and Robinson, *J Chem. Soc.*, 1914, **105**, 2387).

It is obtained in practically quantitative yield by the following method: *o*-Veratraldehyde (100 g.), malonic acid (130 g.), and piperidine (5 c.c.) were heated in pyridine solution (250 c.c) for 1½ hours on the steam-bath, during which rapid elimination of carbon dioxide took place, and the reaction was completed by boiling for 10 minutes on the sand-bath. The product on pouring into excess of dilute hydrochloric acid gave an almost quantitative yield of 2:3-dimethoxycinnamic acid, m.p. 181°.

Nitration of 2:3-*dimethoxy-cinnamic acid in fuming nitric acid.*—Well dried 2:3-dimethoxy-cinnamic acid (1 g.) was added in small portions to fuming nitric acid (*d* 1·5, 40 c.c.) cooled in a freezing mixture, the temperature being kept below 0° throughout the reaction. The reaction mixture was poured over ice and water, rubbed, and filtered after a time. The almost colourless precipitate was dried on porous plate and crystallised from alcohol. The nitration product was thus obtained in beautiful colourless prisms, m.p. 198°, which was not elevated on recrystallisation. (Found: N, 9·4. Dinitro-2:3-dimethoxy-cinnamic acid, $C_{11}H_{10}O_8N_2$ requires N, 9·4 per cent.). This substance turned yellow on exposure to the atmosphere.

Nitration with ordinary nitric acid (*d* 1·42).—(*i*) Nitration with exactly equivalent amount of nitric acid in glacial acetic acid did not take place at the ordinary temperature. When the nitration in acetic acid was attempted at 90°, indefinite mixtures of the unchanged cinnamic acid and the nitrated compound were obtained. (*ii*) 2:3-Dimethoxy-cinnamic acid remains unaffected when added to nitric acid cooled to 10°. (*iii*) Most of the 2:3-dimethoxy-cinnamic acid was nitrated under the following conditions:—2: 3-Dimethoxy-cinnamic acid (10 g.), finely powdered and dried was added in small portions to nitric acid (60 c.c.), the whole being stirred vigorously throughout, and the temperature maintained between 10° and 20°.

After a small amount of 2:3-dimethoxy-cinnamic acid had been added, the nitrated product began to separate and in a short time the whole became a semi-solid mass which had to be stirred vigorously by hand or a powerful motor. The mixture was allowed to remain for 3 hours with stirring, and then diluted with a large amount of ice and water, and the precipitated nitro-compounds were filtered, washed and then dried on the steam-bath.

The separation of the nitration product thus obtained was carried out by the following two methods:—(*i*) The nitration product was repeatedly crystallised from alcohol till an acid melting at 231° was left. The mother-liquors were all mixed together and evaporated down to dryness, and the residue obtained was converted into a mixture of esters by saturating its solution in alcohol (absolute) with dry hydrogen chloride and then boiling it for four hours. The esters thus obtained were separated in the usual manner by careful fractional crystallisations (compare Rubenstein, *loc. cit.*), whereby a less soluble ester, m. p. 116°, was obtained. This crystallises in prisms or prismatic plates. From the more soluble fractions after repeated crystallisation was obtained an ester, m. p. 90°, crystallising in beautiful long needles. For preparation of the acid melting at 231°, which was found to be the 5-nitro-2: 3-dimethoxy-cinnamic acid, this method of separation is most convenient. (*ii*) For effecting a complete separation the following method was found more convenient: The dried mixture of nitro-acids (100 g.), methyl alcohol (600 c.c.), and concentrated sulphuric acid (60 c.c.) were boiled together under reflux for four hours. Methyl alcohol was then removed by distillation, the product diluted with water and neutralised with sodium carbonate, whereby the ester was precipitated. The precipitate was filtered, dried and crystallised from a little alcohol, when the product melted at 128-135°. The whole of the ester obtained (100 g.) was dissolved in a litre of alcohol and allowed to cool, when the crude 5-nitro-2: 3-dimethoxy-cinnamic acid separated first. On crystallising this first fraction thrice, 5-nitro-2: 3-dimethoxy-cinnamic acid methyl ester was obtained pure as beautiful long needles, m. p. 154-5°. The latter fraction obtained from the mother-liquors was then subjected to a series of careful fractional crystallisations, first from alcohol and then from benzene, whereby an ester, m. p. 150°, was obtained, which was found to be methyl 6-nitro-2: 3-dimethoxy-cinnamate crystallising in colourless beautiful long needles. A mixture of the two esters melted about 130°.

The ethyl ester, m. p. 116° and the methyl ester, m. p. 154-5° gave on hydrolysis an acid melting at 231°, which was identical with 5 nitro-2: 3-dimethoxy-cinnamic acid obtained by synthesis, and the two esters were also identical, as shown by mixed melting points, with the corresponding esters prepared from the synthetical 5-nitro-2: 3-dimethoxy-cinnamic acid.

The ethyl ester m. p. 90° and the methyl ester m. p. 150° gave on hydrolysis an acid m. p. 220°, which was identical with 6-nitro-2: 3-dimethoxy-cinnamic acid, and are therefore the ethyl and methyl esters of 6-nitro-2: 3-dimethoxy cinnamic acid. (Found for ethyl ester m. p. 90°: N, 4·9. $C_{13}H_{15}O_6N$ requires N, 5·0 per cent. Found for methyl ester m. p. 150°: N, 5·3. $C_{12}H_{13}O_6N$ requires N, 5·2 per cent.).

6-Nitro-2: 3-dimethoxy-cinnamic acid (XVIII.)—(*i*) 6-Nitro-2: 3-dimethoxy-benzaldehyde (10 g.), malonic acid (11 g.) and piperidine (5 c.c.) were heated in pyridine solution (25 c.c.) for 1½ hours on the steam-bath during which period some elimination of carbon dioxide took place and the liquid turned dark, and then the whole was boiled for a further period of ten minutes. The product on pouring into excess of dilute hydrochloric acid gave a dark mass. After filtration and examination, the dark product proved to be a mixture of two substances, one of which was insoluble in cold sodium carbonate while the other was not. The soluble part was precipitated by acid and crystallised from alcohol with the aid of animal charcoal. It crystallised in colourless needles m. p. 220° and is obviously 6-nitro-2: 3-dimethoxy cinnamic acid. The part that was insoluble in sodium carbonate was a brown amorphous substance, almost insoluble in methyl or ethyl alcohol. It could not be obtained so far in a crystalline state. (*ii*) Most of the 6-nitro 2: 3-dimethoxy-cinnamic acid required for the following experiments was obtained by the hydrolysis of the ester obtained from the mixture of esters of the nitro-compounds obtained by direct nitration of 2: 3-dimethoxy-cinnamic acid as already described. The hydrolysis of the ester is best effected under the following conditions:—

The pure ester (2 g.) was taken up in water (10 c.c.) and to the mixture was added all at once concentrated sulphuric acid (10 c.c.) and the whole shaken vigorously. The ester went into solution (colourless), and the hydrolysis was practically complete in a minute, but still to ensure completion, glacial acetic acid (10 c.c.) was added and the mixture boiled for 5 minutes, during which the nitro-acid began to separate. The reaction product was poured over ice,

allowed to remain for sometime, filtered, washed, dried, and crystallised from alcohol. It crystallises in colourless needles and melts sharply at 220° (compare Rubenstein who described it as a brown substance of m. p. 210-215°, *loc. cit.*). (Found: N, 5·6. $C_{11}H_{11}O_6N$ requires N, 5·5 per cent.). This acid gave the same mixed melting point with the acid obtained by the method (*i*). To obtain further evidence for the constitution of this acid, the acid was oxidized to 6-nitro-2: 3-dimethoxy-benzaldehyde under the following conditions: —6-Nitro-2: 3-dimethoxy-cinnamic acid (0·5 g.) was suspended in water (20 c.c.) and a little sodium carbonate solution (2 c. c.) added and stirred when the nitro-cinnamic acid went in solution. The solution was taken up in a separating funnel mixed with benzene (50 c.c.) and to the mixture was gradually added a cold saturated solution of potassium permanganate (0·7 g. in 11·7 c. c. water). After each addition of permanganate the mixture was vigorously shaken and cooled under the tap. After the addition of all the permanganate the mixture was allowed to remain for a few minutes and then filtered. The precipitate of manganese dioxide was washed with benzene, the benzene layer separated from the aqueous layer, dried over sodium sulphate, and the solvent removed by distillation when an almost colourless residue (0·25 g.) was left. On crystallisation from methyl alcohol or benzene it melted at 110° and a mixed melting point with 6-nitro-2: 3-dimethoxy-benzaldehyde caused no depression.

6-*Amino*-2: 3-*dimethoxy-cinnamic acid* (XIX).—To a solution of ferrous sulphate (recrystallised, 16 g.) in water (30 c. c.) heated up to 90° was added a solution of 6-nitro-2: 3-dimethoxy-cinnamic acid (2 g.) in dilute ammonia. To the mixture heated on the water-bath was then gradually added concentrated ammonia (6 c.c), while the contents were vigorously shaken throughout. After the addition of ammonia the whole was heated for a further ¼ hour, filtered, the filtrate concentrated down to one third its volume, and then carefully made just acid. The amino-acid was precipitated as a crystalline yellow powder. It was recrystallised from boiling water when it was obtained as glistening prisms, m.p. 179°. (Found: N, 6·4. $C_{11}H_{13}O_4N$ requires N, 6·3 per cent.). In contact with hydrochloric acid it readily passes into the hydrochloride. Both the amino acid and its hydrochloride are much more soluble in the usual solvents than its isomer, 5-amino-2:3-dimethoxy-cinnamic acid and its hydrochloride.

6-Cyan-2:3-dimethoxy-cinnamic acid (XX).—A mixture of 6 amino-2:3-dimethoxy-cinnamic acid (2·2 g.), water (11 c.c.) and concentrated hydrochloric acid (2·3 c.c.) was treated at 0° with sodium nitrite (0·75 g.) and the clear diazo solution filtered from a trace of insoluble substance and was added to a hot solution of potassium-cuprous-cyanide, obtained by adding to a solution of copper sulphate (2·5 g. in 15 c.c.) a solution of potassium cyanide (2·8 g. in 5 c.c. water). After the addition of the diazo solution to the potassium cuprous cyanide solution, the mixture was heated for a further quarter of an hour on the water-bath, cooled and made slightly acid by means of concentrated hydrochloric acid. The cyano acid was precipitated. The precipitate was filtered, washed, extracted or shaken up with cold sodium carbonate solution, filtered from a slight amount of undissolved inorganic substance and the clear solution acidified with concentrated hydrochloric acid. The cyano acid thus obtained was collected and crystallised from alcohol with the aid of animal charcoal. It crystallised from alcohol in glistening needles, m.p. 238°. (Found: C, 62·1; H, 4·8. $C_{12}H_{11}NO_4$ requires C 61·8; H, 4·7 per cent.).

Attempts at oxidation of 6-Cyano-2:3-dimethoxy-cinnamic acid to 6-Cyano-2:3-dimethoxy-benzaldehyde.—(*i*) 6-Cyano-2:3-dimethoxy-cinnamic acid (1 g.) was suspended in water (40 c.c.) and a little sodium carbonate solution (5 c.c.) added and stirred when cyano-cinnamic acid went in solution. The solution was taken up in a separating funnel, mixed with benzene (100 c.c.) and to the mixture was gradually added a saturated solution of potassium permanganate (1·4 g. in 23·4 c.c.). After each addition of permanganate the mixture was vigorously shaken and cooled under the tap. After the addition of all the permanganate, the mixture was allowed to remain for a few minutes and then filtered. The precipitate of manganese dioxide was washed with benzene. The benzene layer, separated from the *aqueous-layer* (*A*), was dried over sodium sulphate and the solvent removed, when a colourless residue (0·1 g.) remained. When crystallised from water it came out as needles which turned yellow on exposure to air and light. It shrinks at about 115° and melts completely at about 220°. (Found: C, 53·8; H, 4·2. $C_{10}H_9O_3N$ requires C, 62·8; H, 4·7 per cent.). When crystallized from benzene it came out as a crystalline powder, m.p. about 225°. (Found: N, 7·0 per cent.). (*ii*) The oxidation was next carried out below 0° under conditions essentially similar to the above, but

slight excess of permanganate (1·8 g.) being used. The same product was again obtained. This substance was not hydrolysed to any acid by boiling for four hours with the following hydrolysing agents:—(1) dilute hydrochloric acid, (2) concentrated hydrochloric acid in ethereal solution, (3) 20 per cent. sulphuric acid. It was converted into tarry substances by boiling with a mixture of equal volumes of water, sulphuric acid and glacial acetic acid or by warming with concentrated hydrochloric acid. The substance was also decomposed by boiling with dilute alkali. (*iii*) Attempts to oxidize the cyano-cinnamic-acid to the corresponding cyano-aldehyde by means of alkaline hydrogen peroxide were also unsuccessful.

The *aqueous filtrate* (*A*) obtained in (*i*) and (*ii*) on acidification, did not give any precipitate, so the acidified solution was extracted several times with ether, which however extracted nothing. The aqueous solution was therefore neutralised, and concentrated down and then acidified. Nothing crystallisable was precipitated. In another experiment, the aqueous filtrate (A) was carefully neutralised. The neutral solution does not give any precipitate with barium chloride, lead acetate or silver nitrate.

6-*Carboxy*-2:3-*dimethoxy-cinnamic acid* (XXIII).—6-Cyan-2:3-dimethoxy cinnamic acid (0·5 g.) was boiled for two hours with 10 per cent. sodium hydroxide solution (10 c.c.), cooled and carefully acidified with concentrated hydrochloric acid and kept for twenty-four hours. The crystalline precipitate was collected and crystallised from water with the aid of animal charcoal. It crystallised in beautiful needles, m.p. 194°, and is readily soluble in hot water and alcohol but rather sparingly in ether. (Found: C, 57·3; H, 4·9. $C_{12}H_{12}O_6$ requires C, 57·1; H, 4·8 per cent.).

Oxidation of the carboxy-cinnamic acid.—(*i*) 6-Carboxy-2:3-dimethoxy-cinnamic acid (1 g.) was dissolved in a little dilute sodium carbonate solution and diluted to 40 c.c. A saturated solution of permanganate (1·5 g. in 25 c.c. water) was added very slowly to the solution which was kept below 0° and continually stirred. After remaining for 12 hours, the whole was filtered and acidified when a crystalline precipitate gradually appeared. It crystallised from alcohol in beautiful long needles, m.p. 202°. (Found: C, 55·79, 55·85; H, 4·84, 4·75 per cent.). This substance does not form an oxime and has none of the properties of ψ-opianic acid. The filtrate from the above precipitate was extracted with ether, the ether solution dried, and the ether removed when it was found that ether had

extracted nothing. The filtrate was therefore concentrated down, but nothing definitely crystallisable was obtained. (*ii*) A similar product was obtained when oxidation was carried out with 2 per cent. potassium permanganate solution.

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On the Photochemical Reaction between Glucose and Hydrogen Peroxide in Acid Medium with Tungstic Acid Sol as Photocatalyst. Part I.

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In a previous communication from this laboratory Kappanna (*J. Indian Chem. Soc.*, 1928, **5**, 387) has shown that the oxidation of glucose by iodine depends essentially on the p_H of the medium, and that phosphates regulate the oxidation of glucose only by their action as buffering agents. In the present paper, results of further study on the oxidation of glucose are presented.

It is well known that the reaction between glucose and hydrogen peroxide proceeds quickly in the dark in an alkaline medium but in an acid solution, the velocity of oxidation of glucose by hydrogen peroxide even at 40° is almost negligible (Harden and Henley, *Biochem. J.*, 1921, **15**, 672). This oxidation of glucose by hydrogen peroxide has not been found to be at all sensitive to light. In the presence of tungstic acid sol the rate of oxidation of glucose by hydrogen peroxide is also negligible in the dark, but if the reaction mixture is exposed to radiations in the immediate ultraviolet, the oxidation has been found to proceed with considerable velocity.

Qualitative observations on the photochemical reduction of tungstic acid by celluloses, sugar, glucose, dextrin, etc., have already been made by various investigators.

Sabanejeff found that when sodium metawolframate was treated with excess of hydrochloric acid and dialysed, the sol consisted of particles having the composition Na_2O, $4WO_3$, $2H_2O$. It is curious however that the sol when freshly prepared can reduce grape sugar in presence of light. Whereas on ageing, it ceases to be photosensitive. Wassiljewa (*Z. wiss. Phot.*, 1913, **12**, 1) studied thoroughly this phenomenon of ageing of tungstic acid sol. The velocity of reduction of tungstic acid sol by excess of glucose in presence of radiations from a constant source of light was determined by titrating

the reduced blue compound of tungsten with standard permanganate solution. Wassiljewa assumed that the rate of reduction at any time was a measure of the concentration of photo-sensitive tungstic acid sol present at that time. He concluded that the velocity of transformation of tungstic acid sol from the photosensitive to the photoinsensitive variety followed the unimolecular equation, and he suggests that on ageing, the sol gains in hydration, thus:—

$$Na_2O+4WO_3 \longrightarrow Na_2O,4WO_3,H_2O \longrightarrow Na_2O,4WO_3,2H_2O.$$

It has been observed by the authors, in course of the present investigation, that with excess of glucose, the photochemical reduction of tungstic acid does not proceed to completion, but that depending on the intensity of light the reaction comes to a stop after a certain amount of reduced tungsten compound has been formed. In our investigation the concentration of the reduced blue compound never exceeded an equivalent of $M/150$ potassium permanganate. But if, after the reaction had been brought to a standstill, the light from the mercury lamp was cut off, and a stream of air bubbled through the reduced solution in the quartz tube, until the blue colour disappeared, and then the mixture again exposed to light, the reduction progressed as rapidly as before. Very probably, the cause of this reaction being brought to a stop is to be sought for in the screening effect of the coloured substance from the active radiations. This phenomenon of auto-retardation throws doubt on the validity of the assumption of Wassiljewa that the rate of reduction is a measure of the concentration of the photosensitive sol.

During the process of the photochemical oxidation of glucose by hydrogen peroxide in presence of tungstic acid, the appearance of this blue colour could not be noticed, indicating that the reduced blue compound of tungsten was not formed at all, or that it disappeared as soon as it was formed. The complicated phenomenon of auto-retardation, which is closely associated with the concentration of the reduced blue compound of tungsten, was therefore entirely eliminated in our investigation, and tungstic acid sol behaved as a pure photocatalyst in the oxidation of glucose by hydrogen peroxide. The disturbing effect due to the ageing and the consequent desensitization of the sol is not very perceptible within four hours of the preparation of the sol; and hence all measurements of reaction velocity recorded in this paper were completed within four hours after the preparation of the reaction mixture.

Experimental.

The source of light was a quartz mercury-lamp run at constant values of current and voltage from a storage battery. The reaction mixture was kept inside a quartz tube placed at a constant distance from the light source. The temperature of the mixture was kept constant by enclosing the reaction tube inside a larger quartz tube, the annular space being filled with water which was circulated from a thermostat by means of a pump.

Corning glass filter G. 586 (*vide* Technologic papers of the Bureau of Standards, No. 148) was used for isolating the spectral region 330-430 $\mu\mu$ in the violet and the ultraviolet. These radiations have no action on hydrogen peroxide as such, but the ultraviolet light transmitted by this filter is very effective in bringing about the oxidation of glucose by tungstic acid sol and hydrogen peroxide.

The reaction mixtures used in this investigation are given in the following tables. It will be noticed that the concentration of hydrochloric acid was never less than 0·075N. Sodium tungstate reacts with hydrochloric acid to form a sol according to the equation,

$$4Na_2WO_4 + 6HCl = Na_2O, 4WO_3 + 6NaCl + 3H_2O.$$

In our experiments, therefore, the molar concentration of tungstate was always less than two-thirds the concentration of hydrochloric acid. The reaction mixtures were quite stable in the dark and no visible turbidity due to the coagulation of the tungstic acid sol occurred during the time of carrying out the experiments.

Kingzett's method was adopted for the titration of hydrogen peroxide left over. About 2 grams of potassium iodide were dissolved in 200 c.c. of water and 30 c.c. of H_2SO_4 solution (1:2) added. 2 C.c. of the reaction mixture were taken out, added to this solution, the flask shaken for five minutes, and the amount of iodine liberated titrated with thiosulphate solution. In acid solution the presence of glucose does not affect the titration in the least.

It was necessary also to determine if the hydrogen peroxide undergoing decomposition is used up entirely for the oxidation of glucose, or whether, a part of the hydrogen peroxide decomposes giving rise to free oxygen which escapes in the atmosphere.

Hence attempts were made to ascertain the amount of glucose left over after the completion of each experiment, and compare the amount of glucose oxidised with the amount of hydrogen peroxide decomposed. The method adopted for glucose estimation was the hypoiodite method of Willstätter (*Ber.*, 1918, **51**, 780). The tungstic acid present in the reaction mixture was at first removed by precipitation with barium chloride in approximately neutral solutions. Excess of iodine was then added to the mixture containing glucose and then an equivalent amount of caustic soda solution was added drop by drop to the mixture which was shaken all along. The mixture was then made acidic and the amount of iodine left over was titrated with thiosulphate solution. The alkalinity of the solution during this operation should always be so carefully adjusted that hydrogen peroxide should not undergo spontaneous decomposition with measurable velocity. It may be stated here that oxidation of one molecule of glucose corresponded to the decomposition of one molecule of hydrogen peroxide.

TABLE I.

Composition of the reaction mixture:—
HCl = ·075 N ; Glucose = ·025N ; Sodium tungstate = ·025M.
Hydrogen peroxide (Merck's Perhydrol) = 0·0166M.
Temperature—30·5° ; Spectral region, 330—400 $\mu\mu$.

	Time in minutes.	C.c. of thiosulphate ≡ 2 c.c. of reaction mixture.	K (unimolecular with respect to H_2O_2).
1.	0	5·9	
			·0024 (from 1 & 2)
2.	60	4·35	
			·0041 (from 2 & 3)
3.	120	2·45	
			·0041 (from 2 & 4)
4.	180	1·4	

It will be noticed that there is an induction period at the beginning, but after an hour of exposure, the monomolecular velocity constants with respect to hydrogen peroxide agree very well among themselves.

TABLE II.

Effect of change in the concentration of free hydrochloric acid on the monomolecular velocity constant.

Concentrations of glucose and hydrogen peroxide same as in Table I ; temp. 30·5° ; light same as before.

Conc. of total HCl.	Conc. of free HCl.	Conc. of Na-tungstate.	*K*.
·075 N	·037 N	·025 M	·0041
·108 N	·071 N	·025 M	·0026
·216 N	·180 N	·025 M	·0017
·108 N	·089 N	·0125 M	·0061
·216 N	·197 N	·0125 M	·0040

It will be seen that roughly speaking for the same concentration of tungstic acid, the velocity constants vary inversely as the square root of the concentration of free hydrochloric acid.

TABLE III.

Effect of varying the concentration of sodium tungstate on the velocity of reaction.

Temperature, light intensity, concentrations of glucose and hydrogen peroxide same as in Table I.

Conc. of Na-tungstate	·025 M	·0125 M	·0063 M	·0036 M
Conc. of HCl	·216 N	·216 N	·216 N	·216 N
K (velocity constant)	·0017	·0040	·0055	·0041

The values of the monomolecular constant pass through a maximum as the concentration of sodium tungstate increases.

TABLE IV.

Effect of varying the concentration of glucose on the velocity of reaction.

Temperature, light intensity, concentrations of sodium tungstate, hydrochloric acid, and hydrogen peroxide same as in Table I.

Conc. of glucose ...	·025 M	·0125 M	·0063 M
K ...	·0041	·0040	·0038

The values of K slightly increase as the concentration of glucose increases. In fact $1/K$ when plotted against the inverse of the concentration of glucose gives a fairly good straight line (*vide* Fig. I).

Fig. 1.

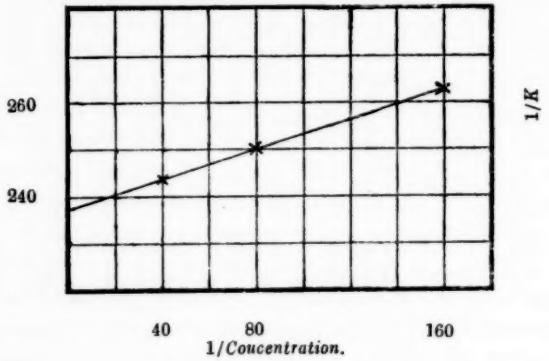

TABLE V.

Temperature coefficient of K.

Light intensity and composition of reaction mixture same as in Table I.

Temp.	30°·5	40°·5
K	·0041	·0053

The value of K increases 1·3 times for a rise in temperature of ten degrees centigrade.

Discussion of Results.

Any mechanism of reaction, which may be proposed for this photochemical oxidation, should be in a position to explain the following facts:—

1. The velocity of reaction with reference to hydrogen peroxide is monomolecular.

2. The velocity constant is, within a certain range, inversely proportional to the concentration of hydrogen ion.

3. The velocity constant is affected to a very small extent by the concentration of glucose.

4. Other conditions remaining the same, the monomolecular velocity constant at first increases with increase in the concentration of sodium tungstate, passes through a maximum and then diminishes rapidly.

It is well known that the particles of a tungstic acid sol are negatively charged and hydrogen ions therefore will be electrically

absorbed on the surface. According to Mukherjee (*Trans. Farad. Soc.*, 1921, **16**, 103), the fraction θ of the original charge on the surface not neutralised by adsorption of monovalent ions is given by the equation $KC\theta^2+\theta-1=0$, where C is the concentration of the monovalent ion. Now if θ be small compared with unity *i.e.*, if the neutralisation of the charge is almost complete, which we may expect when the concentration of the hydrogen ion is not too small,

$$\theta^2=\frac{1}{KC} \text{ or } \theta=\frac{K_1}{\sqrt{C_H}}.$$

If θ is the fraction of the charge not neutralised by hydrogen ions, it follows that θ also represents the fraction of the total surface of the sol particles which remain available for adsorption by other molecular species. The two molecular species which can conceivably get adsorbed on the surface of the sol particles are glucose and hydrogen peroxide. Now it is well known that hydrogen peroxide has great affinity for tungstic acid. Thus it combines with tungstates to form pertungstates, and Pissarjewsky has actually shown from determination of the distribution of hydrogen peroxide between ether and an aqueous solution of sodium tungstate and sulphuric acid that a considerable fraction of hydrogen peroxide in aqueous solution remains combined with tungstic acid (*Z. physikal. Chem.*, 1903, **43**, 166).

It is evident therefore that on the surface of the particles of tungstic acid sol, not already covered with hydrogen ion, the molecules of hydrogen peroxide will get adsorbed to form a peroxide complex. The amount of complex so formed will be proportional to the concentration of hydrogen peroxide and the free surface θ, or

$$\theta_1\left(\begin{array}{c}\text{Fraction of surface}\\ \text{covered with molecules of}\\ \text{hydrogen peroxide.}\end{array}\right)=K_2C_{(H_2O_2)}\cdot\frac{K_1}{\sqrt{C_H}}.$$

The elementary spaces of the peroxide surface get activated under the stimulus of radiation and may oxidise a molecule of glucose which happen to collide against this surface during its life period of excitation. If τ be the life period of the excited peroxide space and T be the interval between two successive collisions of glucose molecules on the same peroxide space, the velocity of oxidation of glucose will be given by the equation,

$$\frac{dx}{dt} = K_3 \frac{\tau}{T+\tau} \cdot \theta_1$$ (the intensity of effective radiation remaining constant).

T, the interval between two successive collisions of the glucose molecule against the peroxide surface will be inversely proportional to the concentration of glucose.

Hence

$$\frac{dx}{dt} = \frac{\tau}{\frac{A}{C_{(\text{Glucose})}} + \tau} \cdot K_3 \cdot K_2 \cdot K_1 \cdot \frac{C_{(H_2O_2)}}{\sqrt{C_{H.}}}.$$

If T or $\frac{A}{C_{(\text{Glucose})}}$ be small compared with τ, $\frac{dx}{dt} = K_4 \cdot \frac{C_{(H_2O_2)}}{\sqrt{C_{H.}}}$

and this is the relation that has been found to hold good in actual experiment. It will also be noticed that the function $\frac{\tau}{\frac{A}{C_{\text{Glucose}}} + \tau}$ is included in the value of K_4, and $1/K_4$ will therefore include the function $\frac{\tau + \frac{A}{C_{(\text{Glucose})}}}{\tau}$

or $$1 + \frac{A}{\tau} \cdot \frac{1}{C_{(\text{Glucose})}}.$$

The value of $1/K_4$ when plotted against the inverse of the concentration of glucose should give a straight line which has also been experimentally realised.

The increase in the value of velocity constant with increase in the concentration of the tungstic acid sol to a maximum and then its rapid diminution as the concentration of the photocatalyst is continuously increased, must await a satisfactory explanation until further investigations in progress are carried out. It may be noted however, that in previous communications from this laboratory on the photochemical transformation of *allo*-cinnamylidene-acetic acid into the normal variety, with iodine as photo-catalyst, a similar variation of velocity constant was noticed and the analogy of this phenomenon with the variation of fluorescent intensity as the concentration of the fluorescing substance is increased was brought out.

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A Study of the Composition of Jute Fibre with Special Reference to the Use of Chlorine Dioxide as an Analytical Reagent.

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Since the epoch-making investigations of Cross and Bevan on jute, little attention has been paid to the systematic study of the chemistry of the fibre which, according to these renowned investigators, constitutes an ideal material for the study of lignocelluloses. The methods of investigation in this field have, in recent years, undergone profound modification in many respects and it is highly desirable to apply these methods to the investigation of jute whose economic importance to this province is well known.

In this work, it is proposed to study the action of chlorine dioxide on jute with a view to determine the composition of the fibre and to compare the results with those obtained by the usual standard methods.

Hugo Muller ("Pflanzenfaser," p. 59; also Cross and Bevan, "Cellulose," 1918, p. 110) gives the following results of the analysis of jute, the figure for raw cellulose being obtained by treatment with bromine water and is hence very low while the figure for incrusting matter is proportionally high.

	Jute almost colourless.	Jute light yellow.
Moisture	9·93 %	9·64 %
Ash	0·68 ,,	...
Water extract	1·03 ,,	1·63 ,,
Fat and wax	0·39 ,,	0·32 ,,
Cellulose (raw)	64·24 ,,	63·05 ,,
Incrusting matter (by difference)	23·73 ,,	25·36 ,,

The most recent analysis of jute is given as follows by Lehne and Scheppmann (*Z. angew. Chem.*, 1925, **38**, 93).

Moisture ...	11·42 %	
Ash	0·73 ,,	(calculated on dry jute).
Water extract ...	3·84 ,,	,, ,, ,,
Fat and resin	1·03 ,,	,, ,, ,,
Cellulose (raw)	78·84 ,,	,, ,, ,,
Lignone	20·98 ,,	,, ,, ,,
Pentosan (furfural) ...	10·25 ,,	,, ,, ,,

The above figure for raw cellulose has been obtained by the chlorination method while lignone has been estimated by the method of Willstätter and Zechmeister.

Schmidt and Graumann (*Ber.*, 1921, **54**, 1860) observed that a solution of chlorine dioxide in water removes lignone without having any injurious effect on the polysaccharides. In the following experiments, the action of chlorine dioxide on jute has been studied and it has been found that both raw cellulose and lignone in jute may be estimated in one and the same operation, when the method of Schmidt and Graumann is modified by avoiding treatment with sodium sulphite. In that case, the figures for lignone agree substantially with those obtained by the standard method of Willstätter and Zechmeister while the figures for raw cellulose are higher than those obtained by the chlorination method. This is not due to any residual lignone in the cellulose but to the fact that the accompanying carbohydrates are very little affected by chlorine dioxide while they are partly destroyed by the chlorination method of Cross and Bevan. This discrepancy in the cellulose content, as determined by these methods, is not however of any material importance. Chlorination has been accepted as a standard method not because it gives a quantitative yield of pure cellulose but that it gives a higher yield of lignone-free raw cellulose than any other method. Not only a part of the hemicellulose is destroyed by the action of chlorine but cellulose itself is susceptible to this reagent. For this reason it will be seen that a higher percentage of α-cellulose is obtainable from jute treated with chlorine dioxide than from Cross and Bevan's jute cellulose.

Analysis of jute fibre.

About one foot from the lowest part of jute and some 2-3 feet from the upper part were rejected. The fibres, freed from woody matter, were cut to small pieces and freed from dust, dirt and adherent tissues by washing with soap. The fibres were then dried and stocked for the purpose of analysis.

Moisture.—Moisture was estimated by drying the fibre at 105° in vacuum over phosphorous pentoxide. The amount of moisture in the fibre was found to vary considerably with atmospheric humidity at different times of the year.

Wt. of air-dry jute (gm.)	Wt. of dried jute. (gm.)	% of moisture.	Remark.
1·6746	1·4986	10·51	Estimated in winter.
1·2576	1·1246	10·57	"
2·0	1·7162	14·19	Estimated in rainy season.

Ash.—Ash was estimated by igniting the jute in a platinum crucible.

Wt. of dry jute. (gm.)	Wt. of ash. (gm.)	% of ash on dry jute.
1·5786	0·0081	0·51
0·8618	0·0044	0·51

Fat and resin.—Fat and resin were estimated by repeated extraction with a mixture of alcohol and benzol (1 : 1).

Wt. of dry jute. (gm.).	Wt. of fat and resin (gm.).	% of fat and resin on dry jute.
6·7368	0·0568	0·843
3·6382	0·0308	0·846

Pentosans.—The pentosans were determined by treating the jute with hydrochloric acid (*d* 1·06) and estimating the furfural as phloroglucide according to the method of Tollens and Bödener (*Z. für Landwirt.*, 1910, **58**, 232).

Wt. of dry jute. (gm.)	Wt. of phloroglucide. (gm.)	Wt. of furfural. (gm.)	% of furfural on dry jute.
1·7162	0·2806	0·1607	9·369
,,	0·2748	0·1574	9·176
,,	0·2792	0·1599	9·322

Raw cellulose.—Raw cellulose is generally estimated directly after the removal of incrusting matters. A large variety of reagents (Cross and Bevan. "Cellulose," 1918, pp. 94-98) are used for the removal of lignone matter from lignocelluloses but all of them act chemically on cellulose matters as well, converting them into oxy- or hydro-celluloses and hydrolysing into soluble sugars. It is therefore a matter of great difficulty to estimate the total amount of cellulose matters. The chlorination method of Cross and Bevan is generally accepted as the best. The following results have been obtained by the use of this method.

Wt. of dry jute. (gm.)	Wt. of raw cellulose (dry). (gm.)	% of raw cellulose on dry jute.
0·7206	0·5434	75·40
0·6880	0·5119	74·40
0·6195	0·4734	76·40
0·6079	0·4505	74·10
0·4812	0·3571	74·20

Chlorine dioxide as a reagent for the estimation of raw cellulose.

It has already been inicated that chlorine attacks cellulose matters besides lignone. The chlorination method of Cross and Bevan cannot therefore be expected to give quantitative yield of cellulose matters,

In the following experiments, the action of chlorine dioxide is studied from a quantitative point of view and it is found that a much higher yield of raw cellulose is thus obtained, the accompanying polysaccharides being practically unaffected by this reagent.

In preparation of chlorine dioxide solution and in determining its strength, the directions of Schmidt and Graumann have generally been followed (*Ber.*, 1923, **56**, 23; 1921, **54**, 1862).

Procedure.—A weighed quantity of jute fibre was immersed in chlorine dioxide solution of known strength, free from any trace of chlorine, in a hydrogen peroxide bottle which was then stoppered, shaken thoroughly and kept in the dark at room temperature. The bottle was shaken occasionally and a sample of jute taken out and examined for lignone from time to time. This was done qualitatively with the help of the microscope, while quantitatively lignone was estimated by the well-known method of Willstätter and Zechmister. The lignone matter when acted on by chlorine dioxide became mostly soluble in water and the rest was easily loosened from the fibres which were then shaken with excess of water and washed thoroughly until the washings were perfectly clear and free from any trace of chlorine. The fibre was then pressed on a Buchner funnel and dried in the sun. The fibre thus obtained was almost white in colour, had good tensile strength, though it turned yellowish on prolonged exposure to air. In order to study the best conditions for delignification, the fibre was subjected to the action of chlorine dioxide of different strengths and for different periods of time. As in the case of chlorination, the best results were obtained by repeated treatment with chlorine dioxide solution, though in this case two treatments were found generally sufficient.

TABLE I.

Effect of time on delignification of jute fibre by means of a single treatment *with chlorine dioxide solution.*

Strength of the solution = 2·5 %. Volume of the solution = 350 c.c.

Wt. of dry jute. (gm.)	Time of treatment (hours).	Wt. of raw cellulose (dry). (gm.)	% of cellulose (on dry jute).	% of lignone in the cellulose thus obtd.
22·3575	24	19·3159	86·4	2·01
,,	48	19·0285	85·17	0·79
,,	72	19·0	85·0	0·63

TABLE II.

Effect of repeated *treatments with chlorine dioxide solution of different strengths.*

Period of each treatment is 24 hours.

Strength of ClO_2 solution %	Volume (c.c).	No. of treatments.	Wt. of dry jute (gm.)	Wt. of raw cellulose (dry). (gm.)	% of raw cellulose.	% of lignone in raw cellulose.
0·31	130	1	6·3657	5·7989	91·1	8·26
,,	,,	2	6·2523	5·5120	88·16	4·79
,,	270	3	11·5756	9·9618	86·0	1·83
0·62	130	1	6·6981	5·9841	89·34	4·83
,,	,,	2	6·2121	5·3840	86·67	2·18
,,	200	3	8·2243	6·8471	83·25	1·66
1·25	120	1	4·8125	4·1915	87·10	2·67
,,	,,	2	4·6953	4·0384	86·01	1·78
,,	,,	3	4·6414	3·9834	85·83	1·40
2·5	350	1	22·3575	19·3159	86·4	2·01
,,	,,	2	22·3575	19·0039	85·0	0·603
,,	,,	3	22·8055	19·3391	84·8	0·54

From the above tables it may be observed that delignification may be effected either by prolonged treatment or by repeated action of chlorine dioxide solution of 2·5% strength.

By comparing the above figures of cellulose content with those obtained by the chlorination method it will be noticed that the yield by chlorine dioxide method is about 10% higher. The high α-cellulose and furfural contents in the cellulose thus obtained indicate that the cellulose and hemicelluloses are very little affected by this reagent while the good tensile strength of the treated fibre indicates that the gummy matter is also intact. The fibre crumbles to ultimate cells when boiled with alkaline substances or with sodium sulphite. The initial white colour of the delignified fibre however slowly gives place to a light yellow colour, though when analysed by Willstätter and Zechmeister's method, only traces of lignone can be detected. As the loss in the weight of the treated fibre is equivalent to the lignone content of jute, it is reasonable to assume that practically all

the ingredients present in the original jute with the exception of lignone are also present in the delignified fibre which is therefore an eminently suitable material for the investigation of the composition of jute.

Besides keeping the cellulose matters intact, the chlorine peroxide treatment requires less time and attention and is very simple to carry out.

Lignone.—Of the various methods for the estimation of lignone only a few are of practical importance. These consist of the direct methods of (1) treatment with 42% hydrochloric acid, (2) treatment with 72% sulphuric acid at room temperature and (3) treatment with 1% hydrochloric acid under 6 atmospheres pressure and (4) the indirect method of estimating methoxyl according to the method of Zeisel. In all these methods, the cellulose has to be completely destroyed. The quantitative removal of lignone with the preservation of cellulose always removes a part of the cellulose matters and thus makes the estimation of lignone unreliable. The following figures for lignone content of jute have been obtained by Willstätter and Zechmeister's method as modified by Krall ("Schwalbe and Sieber-Betriebs-Kentrolle in der Zellstoff und Papier-Industrie," p. 102).

Wt. of dry jute (gm.).	Wt. of lignone (gm.).	% of lignone (on dry jute).	Mean percentage of lignone.
4·4715	0·7038	15·74	
,,	0·6842	15·30	15·524
,,	0·6952	15·532	

Chlorine dioxide as a reagent for the estimation of lignone.

The following figures for lignone content in jute have been obtained by treatment of jute with 2·5% chlorine dioxide solution, the procedure being the same as described in the case of cellulose estimation. It will be seen that the results are in fair agreement with those obtained by Willstätter's method, which, for the sake of comparison, is noted in the last column of the following table.

TABLE III.

Wt. of dry jute (gm.).	Wt. of treated jute (gm.).	Loss of weight (lignone) %.	Lignone by Willstätter's method.
22·3575	19·00	15·0	15·524 %
,,	19·0039	15·0	,,
22·8055	19·3391	15·2	,,

It will be observed that this is the only method for the estimation of lignone which works without destruction of cellulose matter and that both cellulose and lignone may be estimated in one and the same operation. The removal of lignone is better and quicker when the fibre is freed from fat and resin by previous extraction with benzol-alcohol. As in the case of cellulose, treatment with sodium sulphite or even with boiling water has to be avoided.

Composition of cellulose fibre obtained from jute by chlorine dioxide treatment.

The cellulose obtained by chlorine dioxide treatment consists of α-cellulose, hemicellulose (pentosans and hexosans) including gummy matter and some pectin substances. Any nitrogenous matter present in jute, would also be present in the fibre as proteins are not attacked by chlorine dioxide (Euler, *Cellulosechem.*, **4**, 109).

The following table gives the characteristic colour tests of the fibre obtained by chlorine dioxide treatment, when observed under the microscope. It gives all the standard colour reactions of cellulose.

TABLE IV.

Reagent.	Cotton.	Raw jute.	Chlorine dioxide treated fibre.
Iodine solution ...	No coloration	Greenish yellow.	No coloration.
Phloroglucinol-hydrochloric acid.	,,	Bright reddish violet.	,,
Zinc chloride—iodine solution.	Violet ...	Greenish yellow.	Violet.

When the fibre was treated with Schweitzer's reagent, it swelled and ultimately dissolved to a viscous solution, but little change of jute under similar condition was observed.

Estimation of moisture in raw cellulose.

Wt. of raw cellulose (air dry) (gm.).	Wt. of moisture. (gm.)	% of moisture.	Remark.
1·1822	0·1041	8·8	Estimated in winter.
0·8591	0·0756	8·8	,,
0·8352	0·1053	12·64	Estimated in the rainy season.

Estimation of ash in raw cellulose.

Wt. of raw cellulose (dry) (gm.).	Wt. of ash. (gm.)	% of ash on dry raw cellulose.
0·5782	0·0019	0·328
0·7934	0·0026	0·327

Estimation of α-cellulose in raw cellulose.—The α-cellulose was determined by treatment with cold caustic soda solution of 17·5% (Jentgen, *Kunststoffe*, 1911, **1**, 165). A weighed quantity of the cellulose fibre was rubbed in a mortar with 17·5% caustic soda solution, allowed to stand for half an hour and diluted with water. The whole mass was then sucked through a linen filter in a Buchner funnel. The residue was washed thoroughly with water until completely free from alkali. Finally it was washed with hot dilute acetic acid and again with water, dried and weighed.

This method of estimating α-cellulose is not above criticism, as the alkali of such strength may convert the cellulose into alkali-soluble oxycellulose and into the highly voluminous cellulose hydrate. But as the other methods of removing hemicelluloses by hydrolysis with weak acids, either alone or in presence of glycerine, attack the α-cellulose strongly, this alkali treatment remains the best method for the estimation of α-cellulose.

TABLE V.

Lignone content of the raw cellulose is 0·54%.

Wt. of dry raw cellulose. (gm.)	Wt. of dry α-cellulose. (gm.)	% of α-cellulose on raw cellulose.	% of α-cellulose on dry jute.
0·5521	0·3950	71·545	60·677
0·5715	0·4085	71·478	60·608

It may be pointed out that this method gives a higher yield of α-cellulose than the chlorination method, and is therefore to be preferred in the quantitative estimation of α-cellulose. In the chlorination method, the halogen evidently attacks not only the hemicellulose to a more or less extent, but the α-cellulose also, as will be seen from the following table.

TABLE VI.

Determination of α-cellulose from the raw cellulose obtained by chlorination method.

Wt. of dry raw cellulose. (gm.)	Wt. of dry α-cellulose. (gm.)	% of α-cellulose on raw cellulose.	% of α-cellulose on dry jute.
0·5434	0·4154	76·44	57·646
0·4505	0·3515	78·02	57·82

In order to test the purity of α-cellulose from raw cellulose, obtained by chlorine dioxide treatment, its ash and furfural contents have been determined and are given in the following tables.

TABLE VII.

Ash in α-cellulose.

Wt. of α-cellulose. (gm.)	Wt. of ash. (gm.)	% of ash on α-cellulose.
0·9893	0·0014	0·141
0·8421	0·0012	0·142

TABLE VIII.

Furfural in α-cellulose.

Wt. of α-cellulose. (gm.)	Wt. of phloroglucide. (gm.)	Wt. of furfural. (gm.)	% of furfural on α-cellulose.
1·8113	0·0334	0·0196	1·082
2·0747	0·0381	0·0225	1·084

The α-cellulose obtained by chlorine dioxide method is evidently purer than that obtained by Lehne and Scheppmann from jute by chlorination method, which gave 2·4% furfuroids (*loc. cit.*).

Hemicellulose in raw cellulose.

It has already been shown that hemicellulose is not removed by the chlorine dioxide treatment so long as the treatment with sodium sulphite is avoided. The hemicellulose can therefore be easily estimated by taking the difference between total cellulose

and α-cellulose. It is to be noted that the quantitative methods for the determination of hemicellulose are at present far from being satisfactory. This is due to the fact that the hemicellulose is attacked and removed along with lignone by all other methods of delignification. This method will, therefore, be of great service in the estimation of hemicelluloses as well as for the investigation of their constitution and chemical properties. The result obtained is, however, slightly higher than the actual amount of hemicellulose, owing to the presence of small amount of lignone (0·54%) and any protein or pectin matter that might be present in the raw cellulose.

TABLE IX.

Wt. of raw cellulose dry (gm.).	Wt. of α-cellulose. (gm.)	Wt. of hemi-cellulose. (gm.)	% of hemi-cellulose on raw cellulose.	% of hemi-cellulose on dry jute.
0·5521	0·3950	0·1571	28·45	24·13
0·5715	0·4085	0·1630	28·52	24·18

Pentosans in raw cellulose.

That the pentosan content of jute fibre has not been materially attacked or removed by treatment with chlorine dioxide is shown by the estimation of the furfural content of the original jute as well as of the raw cellulose. The estimations were carried out as before.

TABLE X.

Wt. of raw cellulose (gm.)	Wt. of phloroglucide (gm.)	Wt. of furfural (gm.)	% of furfural on raw cellulose.
1·7120	0·3000	0·1718	10·04
1·7974	0·3160	0·1776	9·88
1·7260	0·2996	0·1716	9·94

It will be seen that very little of the pentosan matter has been removed ; thus taking the furfural content of jute (lignone, 15·524%) as 9·2%, the calculated furfural content of the delignified fibre is approximately 10·8% whereas about 10% furfural was actually found above. In the chlorination method, however, the pentosans are considerably removed, as is shown by their furfural content. Thus Cross and Bevan state that their raw jute cellulose gave only 4·8%

furfuroids. Lehne and Scheppmann obtained about 10·5% furfuroids in jute (lignone content being 20·98%), and 8·3% in the raw cellulose obtained by chlorination method. If the pentosans were quite unaffected by chlorination, the furfuroids in the delignified jute would amount to 13·3%, while actually they found 8·3%. Evidently a considerable amount of pentosans was removed by the chlorination method followed by them.

Estimation of gummy matter in raw cellulose.

Gummy matter is generally estimated in raw cellulose, isolated from lignocellulose and not in the crude fibre itself. The general method used is that of Kast ("Untersuchung der Spring- und Zundstoffe," 1909, p. 919) which consists in treating cellulose with 5% caustic soda solution. An alkali of this strength would dissolve part of the lignone matter, in addition to the gummy substance, which being protected by lignone would only be incompletely extracted, and would thus vitiate the result. In the isolation of the cellulose matter by usual methods, however, wood gum is largely affected and removed. This is particularly the case when the fibre is washed with alkaline materials or sodium sulphite solution. For these reasons the cellulose obtained from lignocelluloses by the ordinary methods is obtained in the form of ultimate cells. This cellulose material cannot, therefore, be expected to give a quantitative yield of the gummy matter. By the chlorine dioxide treatment, however, the delignified fibre retains its original tensile strength, and evidently the gummy substance, and is reduced to ultimate cells only when boiled with dilute sodium sulphite solution, soda and other alkaline substances. This substance is, therefore, eminently suitable for the quantitative determination of the gummy substance, as well as for the investigation of its chemical nature.

Procedure.—A weighed quantity of the raw cellulose fibre (about 15 gms.) was taken in a conical flask and covered with 300 c.c. of exactly 5% caustic soda solution. The whole was then allowed to stand for 24 hours with frequent shaking. The liquid was filtered and the residue washed with water, the washings being added to the filtrate, which was made up to a definite volume (400 c.c.). To a small amount of the filtrate (100 c.c.) about thrice the volume of rectified spirit was added and the liquid shaken vigorously. It was then neutralised with *N*-hydrochloric acid using phenolphthalein as

the indicator. The acid was then added in slight excess, and the precipitate was allowed to settle for 24 hours, collected on a dried and weighed filter, washed with rectified spirit and ether and was finally dried. To purify the gummy matter thus obtained, it was powdered and dissolved in dilute alkali. The solution was neutralised with *N*-hydrochloric acid, and the gummy substance reprecipitated by rectified spirit, washed as before, and dried. The gummy matter, thus obtained, was a white amorphous substance.

Wt. of dry cellulose (raw) in gm.	Vol. of filtrate in c.c.	Wt. of gum (gm.)	Total wt. of gum (gm.)	% of gum on raw cellulose.	% of gum on jute.
14·9202	100	0·5048			
	,,	0·5052			
	,,	0·4970	2·023	13·56	11·49
	,,	0·5160			

The gummy matter, isolated in the above manner, is not a homogeneous substance, but is mainly composed of pentosans (and hexosans), mixed perhaps with a small amount of pectin matter. This is indicated by the estimations of furfuroids as well as methoxyl.

TABLE XI.

Furfural in the gummy matter.

Wt. of gum. (gm).	Wt. of phloroglucide. (gm.)	Wt. of furfural. (gm.)	% of furfural on gum.
1·3076	0·949	0·5425	41·48
0·8450	0·600	0·3431	40·61

Methoxyl in the gummy matter.

Methoxyl was estimated by treating the gum with hydriodic acid according to the well-known Zeisel's method.

TABLE XII.

Wt. of gum. (gm.)	Wt of silver-iodide. (gm)	% of methoxyl.
0·366	0·0746	2·688
0·333	0·068	2·693

It is important to study the physical and chemical properties of this gummy substance thoroughly, as the tensile strength and other

physical properties of jute, which determine the industrial importance of the fibre, depend very largely on this gummy matter.

Attempts were made to make the delignified fibre less susceptible to the action of alkali, but without success. It is only when a small percentage of lignone matter is present, and thus protects the gummy substance that the fibre can stand a certain extent of washing with slightly alkaline matter. It has been observed that when a minimum amount of 4·79% lignone matter is present in the fibre it is not very susceptible to washing. Whether a fibre with this lignone content is suitable enough for textile purposes, can be determined only by actual spinning tests. The completely delignified fibre, obtained by washing with chlorine dioxide, is of practically white colour, and may, perhaps, be used as a substitute for cotton where little or no washing is necessary.

Summary.

1. It has been found that the highest percentage of raw cellulose is obtained from jute by washing with 2·5% aqueous chlorine dioxide solution without subsequent washing with sodium sulphite.

2. Estimation of lignone and cellulose matters may be made simultaneously in the above operation, and thus save time and expense. The figures for lignone, obtained by this method, agree substantially with those obtained by Willstätter's method.

3. A method has been developed for the quantitative estimation of hemicellulose, and of the gummy substance in jute, as they are not affected in any appreciable degree by the above treatment. For this reason, this is a very suitable material for the isolation and investigation of the chemical nature of these substances.

4. The chlorine dioxide treatment gives higher yield of α-cellulose than the chlorination method, and is therefore to be preferred for this purpose to the chlorination method.

5. The ash and furfural contents of α-cellulose, isolated in the above process, are extremely small, and thus testify to the purity of the α-cellulose.

6. Delignified jute with some 4-5% lignone has been found less susceptible to washing than the completely delignified fibre.

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Substances related to Cochinillic and Carminic Acids. Part II. A Synthesis of α-Coccinic Acid (*m*-Oxyuvitic Acid).

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It was found by the authors (*J. Chem. Soc.*, 1921, **119**, 201 ; *J. Indian Chem. Soc.*, 1925, **2**, 4) and also by Schleussner and Voswinckel (*Annalen*, 1921, **422**, 111) that the condensation of chloral with *m*-cresotic acid produces a complex mixture of substances. The authors, because it appeared to them that this complexity depended largely on the activity of the hydroxyl group in the *m*- cresotic acid, decided to study the condensation of chloral with the methyl ether of this acid, that is, with 2-methoxy-*p*-toluic acid. The main product of this condensation was found to be 2-methyl-5-carboxy-4-methoxy-1-α-hydroxy-βββ-trichloro-ethylbenzene I. This on reduction gave 2-methyl-5-carboxy-4-methoxy-1-ββ-dichloroethyl benzene, II (*J. Indian Chem. Soc., loc. cit.*).

This condensation has now been more fully investigated. It is found that there are produced, in addition to I, the substance III (2-methyl-5-carboxy-4-methoxy-1-αβββ-tetrachloroethyl benzene) and a sulphonic acid, which is IV (2-methyl-5-carboxy-4-methoxy-3-sulpho-1-α-hydroxy-βββ-trichloroethyl benzene).

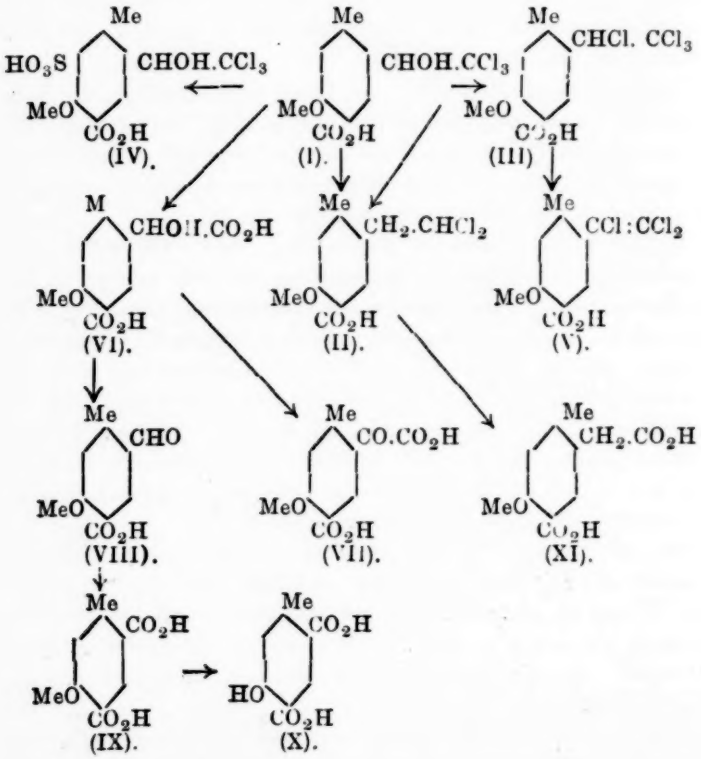
Chattaway and Calvet (*J. Chem. Soc.*, 1928, **133**, 2914) have obtained from chloral and *p*-nitroanisole, as the sole product of the reaction, a substance that contains the same group, $-CHCl.CCl_3$, as is present in III. The authors find that the substance III is produced, in small amount, along with I. It can be obtained from I (*a*) by dissolving in sulphuric acid and passing in hydrochloric acid gas ; (*b*) on heating I with sulphuric acid on the water-bath for about 10 minutes. Each substance, I and III, can be reduced to the same substance II. Under treatment with potassium hydroxide solution the substance III yields the trichlorostyrene V.

The substance I, on hydrolysis of the $-CCl_3$ group, yields the mandelic acid VI, which gives (*i*) on oxidation, the phenyl-glyoxylic acid VII, and (*ii*) on treatment with sulphuric acid, with loss of carbon monoxide, the aldehyde VIII. This aldehyde, on oxidation, gives the methyl ether of α-coccinic acid IX, and this, on hydrolysis, gives α-coccinic acid, X.

Oppenheim and Pfaff prepared α-coccinic acid (*m*-oxyuvitic acid) from ethyl acetoacetate and chloroform (*Ber.*, 1874, **7**, 929). The

same acid was subsequently obtained by Liebermann and Voswinckel as a degradation product of cochinillic acid and was named α-coccinic acid (*Ber.*, 1897, **30**, 1733). The melting point of this substance was doubtful: Beilstein says 295-298° (*Handbuch der Org. Chemie*, 1927, **10**, 512): Claisen observed 310° as the temperature of decomposition (*Annalen*, 1897, **297**, 44). The authors found that α-coccinic acid, obtained as described in this paper, and by the method of Oppenheim and Pfaff, melted at 320-322° with decomposition. The specimen, obtained by the latter method, was methylated and was found to be identical with the methyl ether of α-coccinic acid already prepared.

The substance II on treatment with sulphuric acid undergoes a change in which the group $-CH_2.CHCl_2$, by hydrolysis and oxidation, becomes $CH_2.CO_2H$. This remarkable change was first observed by Meldrum and Vaidyanathan in work not yet published: it affords a valuable means of producing substituted phenylacetic acids, *e.g.*, XI.



Experimental.

2-Methyl-5-carboxy-4-methoxy-1-α-hydroxy-βββ-trichloroethyl benzene (I), *2-Methyl-5-carboxy-4-methoxy-1-αββ-tetrachloroethyl benzene* (III) *and 2-Methyl-5-carboxy-4-methoxy-3-sulpho-1-α-hydroxy-βββ-trichloroethyl benzene* (IV).

2-Methyl-5-carboxy-4-methoxy-1-α-hydroxy-βββ-trichloroethyl benzene has been already described (*J. Indian Chem. Soc., loc. cit.*). The authors have now been able to obtain this compound in larger yield (52 per cent.) along with the substances III and IV.

2-Methoxy-*p*-toluic acid (20 g.), chloral hydrate (24 g.) and sulphuric acid (96-97 per cent., 40 c.c.) were mixed. After 7 days the mixture was poured into water containing ice when a white solid separated (30 g.). The mother-liquor (A) was worked up separately (see below). A solution of this solid in glacial acetic acid gave about 20 grams of I and the mother-liquor gave substance III (1·5 g.) which crystallised from alcohol in rectangular plates, m. p. 200-201°. (Found: Cl, 42·57. $C_{11}H_{10}O_3Cl_4$ requires Cl, 42·73 per cent.)

The substance III was obtained more quikely in two ways : (*a*) The trichloromethyl carbinol I (1 g) was dissolved in sulphuric acid (10 c.c.) and the solution was saturated with hydrogen chloride and left for a day at ordinary temperature ; (*b*) the trichloromethyl carbinol I (4 g.) was dissolved in sulphuric acid (40 c.c.) and the solution was heated on the water-bath for 10 minutes. In each case the solution was poured into water and the solid that separated was crystallised from alcohol. [Yield (*a*) 0·3 g., m. p. 200-201° ; (*b*) yield 2·4 g., m. p. 200-201°.] The substance III on reduction with zinc dust and acetic acid yielded II.

Formation of αββ-Trichloro-2-methyl-5-carboxy-4-methoxystyrene (V).—The tetrachloro compound (1 g.) was heated for about 15 minutes with potassium hydroxide solution (20 per cent., 25 c.c.). After cooling, the solution was acidified with hydrochloric acid. The product crystallised from dilute alcohol in plates, m. p. 185-187°. (Found: Cl, 36·21; equivalent, 295·1. $C_{11}H_9O_3Cl_3$ requires Cl, 36·06 per cent.; equivalent, 295·4.)

The sulphuric acid mother-liquor (A) was neutralised with $BaCO_3$. The clear solution was evaporated on the water bath when a precipitate was formed which was found to be a mixture of $BaSO_4$ and the barium salt of the condensation product I. The mixture was filtered and the clear solution was kept in an evacuated desiccater over

H_2SO_4. The *barium* salt of IV crystallises in silky needles. (Found: Ba, 25·74. $C_{11}H_9O_7Cl_3SBa$ requires Ba, 25·98 per cent.)

2-*Methyl-5-carboxy-4-methoxymandelic acid* (VI).—The trichloromethyl carbinol I (10 g.) was boiled for an hour with a solution of barium hydroxide (50 g.) in water (200 c.c.). The mixture was filtered and the filtrate on cooling yielded the barium salt of the mandelic acid (VI). The filtrate on evaporation gave a further yield of the *barium* salt in tiny needles. (Found: Ba, 30·7. $C_{11}H_{10}O_6Ba$, $4H_2O$ requires Ba, 30·7 per cent.) The salt was acidified with hydrochloric acid until a clear solution was obtained. Barium was removed as $BaSO_4$ and the filtrate was evaporated to small bulk. The hydroxy acid crystallises very slowly and even after seeding takes generally more than 12 hours to get the maximum yield of 6 grams. Recrystallised from ethyl acetate, in tiny groups of needles, it sinters at 95-100° and melts at 105 110° with effervescence. The crystals contain 1 molecule of water. When the substance is dried at 70-80° it melts at 162-163°. (The hydrated substance, found: equivalent, 129·2; H_2O, 7·3. $C_{11}H_{12}O_6,H_2O$ requires equivalent, 129·05; H_2O, 7 per cent. The anhydrous substance, found: equivalent, 120·3. $C_{11}H_{12}O_6$ requires 120·05.)

2-*Methyl-5-carboxy-4-methoxyphenylglyoxylic acid* (VII).—The hydroxy acid just described (1 g.) was dissolved in potassium hydroxide solution: potassium permanganate (1 g.) dissolved in water (40 c.c) was added. Oxidation takes place easily and is over in about half an hour. The mixture was filtered and the filtrate was reduced to a small bulk and then acidified. The substance was recrystallised from hot water in needles, m.p. 211-212°. (Found: equivalent, 119·4. $C_{11}H_{10}O_6$ requires 119·06.) The *barium* salt (microcrystalline) is very sparingly soluble in water. (Found: Ba, 33·68. $C_{11}H_8O_6Ba,2H_2O$ requires Ba, 33·57 per cent.)

2-*Methyl-5-carboxy-4-methoxybenzaldehyde* (VIII).—The hydroxy acid (1·5 g.) was heated with sulphuric acid (97 per cent., 4 c.c.) at 80-100°. Carbon monoxide was evolved during about 15 minutes. The solution was then poured into water (25 c.c.). The aldehyde separated in needles: it was first crystallised from acetic acid and then from water for analysis: m. p. 176-177°. (Found: equivalent, 193·8. $C_{10}H_{10}O_4$ requires 194·04.)

α-Coccinic acid methyl ether (IX).—The aldehyde just described (1 g.) was dissolved in just sufficient potassium hydroxide solution: potassium permanganate (0·5 g.), dissolved in water (25 c.c.), was

added. Oxidation proceeded rapidly and was complete in about half an hour. The mixture was filtered and the filtrate was reduced to small bulk and then acidified. The acid was crystallised from acetic acid and then from methyl alcohol in tiny groups of needles, m. p. 250-252°. (Found: equivalent, 105·3. $C_{10}H_{10}O_5$ requires 105·04.)

The methyl ether of α-coccinic acid was also obtained by oxidation of the trichloromethyl carbinol I. The latter (1 g.) was dissolved in potassium hydroxide solution: potassium permanganate (1 g.) dissolved in water (100 c.c.) was added and the mixture was heated on the water-bath for an hour. After removal of manganese oxide, the solution was reduced to small bulk and then acidified. The product was found to be identical with the α-coccinic acid methylether already obtained. (Found: equivalent, 104·5. $C_{10}H_{10}O_5$ requires 105·04).

α-Coccinic acid (X).—The methylether of α-coccinic acid (0·5 g.) was heated with hydriodic acid (10 per cent., 25 c.c.) under reflux for an hour. On cooling α-coccinic acid separated: it crystallised from acetic acid in shining plates: m. p. 320-322° with decomposition. For verification, the barium salt was prepared, purified and analysed (see below). The acid liberated from this salt was recrystallised from alcohol: m. p. 320-322° with decomposition. (Found: equivalent, 98·2. $C_9H_8O_5$ requires 98·03). The *calcium* salt (needles) crystallises with 4 molecules of water, of which $2\frac{1}{2}$ molecules can be removed at 110-115°. (Found: Ca, 13·2. $C_9H_6O_5Ca,4H_2O$ requires 13·1 per cent.) After heating at 110-115° to constant weight, Ca, 15·51. $C_9H_6O_5Ca,1\frac{1}{2}H_2O$ requires 15·35 per cent.) The *barium* salt (prismatic needles) crystallises with 2 molecules of water, of which $\frac{1}{2}$ molecule can be removed at 110-125°. (Found: Ba, 37·7. $C_9H_6O_5Ba,2H_2O$ requires 37·4 per cent.) After heating at 110-115° to constant weight, found: Ba, 38·08. $C_9H_6O_5Ba,1\frac{1}{2}H_2O$ requires 38·33 per cent.)

α-Coccinic acid was reported to melt at a temperature as low as 298° and as high as 310°. The acid was therefore prepared according to the method of Oppenheim and Pfaff from ethyl acetoacetate and chloroform in presence of sodium ethylate. α-Coccinic acid obtained in this way was impure. It was, therefore, converted into the barium salt, and a solution of this salt, after treatment with animal charcoal was acidified. The resulting solid having been found to be identical (m. p. 320-22° with decomposition) with the α-coccinic acid already prepared was methylated. The methylated product

melted at 250-52° and was identical with the methyl ether of α-coccinic acid already obtained.

2-*Methyl-5-carboxy-4-methoxy-phenylacetic acid* (XI).—2-Methyl-5-carboxy-4-methoxy-1-ββ-dichloroethylbenzene II (1 g.) was heated with concentrated sulphuric acid (5 c.c.) at 70-80° for about an hour: HCl was evolved during the course of the reaction. The mixture was then poured into water (25 c.c.) when some unchanged substance separated which was removed. The filtrate on standing for about 2 days gave crystals (leaflets) which, on recrystallising from water, melted at 164-65°. (Found: equivalent, 112·7. $C_{11}H_{12}O_5$ requires 112·05.)

The *barium* salt (white leaflets) crystallises with $1\frac{1}{2}$ molecules of water. (Found: Ba, 35·6. $C_{11}H_{10}O_5Ba$, $1\frac{1}{2}H_2O$ requires 35·56 per cent.)

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Qualitative Analysis of a Mixture of Ferrocyanide, Ferricyanide and Thiocyanate.

By Pares Chandra Banerjee.

Two methods are now generally employed for the qualitative analysis of a mixture of ferrocyanide, ferricyanide and thiocyanate. Of these, one depends on the use of iron salts while the other devised by Browning and Palmer (*Z. anorg. Chem.*, 1907, **54**, 315) requires solutions of thorium nitrate and cadmium chloride for the separation of ferro- and ferri-cyanide respectively. The second method, though it gives fairly good results, presents some difficulties in the course of filtration, thorium ferrocyanide and cadmium ferricyanide, being in a very fine state of division, easily pass through the filter paper.

The object of the present investigation was to see whether the salts of common metals can be used in place of thorium nitrate. But on studying the solubilities of different ferro- and ferri-cyanide, it has been observed that the metals which give insoluble ferrocyanides also give insoluble ferricyanides. So it is not possible to separate the two acids with the help of these salts.

It has, however, been found that if cerous nitrate whose ferrocyanide is insoluble (100 gms. of water dissolving 0·0017 gm. of cerous ferrocyanide at 21°) is used in place of thorium nitrate, a more granular precipitate of cerous ferrocyanide is formed which can be easily filtered and washed in a comparatively shorter time. On the other hand ferricyanide can be better precipitated as nickel ferricyanide (a substance quite insoluble in water), with a solution of nickel nitrate, which, though a little difficult to wash on account of its gelat' .ous character, does not pass through the filter paper.

Experimental.

In actual analysis 5-10 c.c. of a neutral solution containing potassium ferrocyanide, potassium ferricyanide and potassium thiocyanate were treated in the cold with a solution of cerous nitrate ("Kahlbaum" refined) which gave a crystalline granular precipitate of

cerous ferrocyanide $CeKFe(CN)_6$ (Robinson, *J. Chem. Soc.*, 1909, **95**, 1353). The precipitate was washed with cold water, treated with a little sodium hydroxide solution on the filter paper to decompose the ferrocyanide and to have some sodium ferrocyanide in the filtrate. The solution thus obtained was acidified with hydrochloric acid, and a few drops of ferric chloride were added to it when the formation of Prussian blue indicated the presence of ferrocyanide.

The filtrate left after the separation of ferrocyanide was treated with a slight excess of nickel nitrate when nickel ferricyanide $Ni_3[FeCy_6]_2$, $18H_2O$ was precipitated. The precipitate was, as before, washed with cold water, treated with sodium hydroxide solution to get some sodium ferricyanide, the filtrate acidified and a few drops of ferrous sulphate solution added to it. Formation of Turnbull's blue showed the presence of ferricyanogen ion.

Thiocyanate was detected in the filtrate left after the separation of ferricyanide by adding a few drops of ferric chloride.

Some of the experimental results are shown in the following tables.

TABLE I.

Concentration of $K_4Fe(CN)_6$.	Concentration of $K_3Fe(CN)_6$.	Concentration of KCNS.	Reaction for $K_4Fe(CN)_6$.
0·01 gm.	0·1 gm.	0·1 ,,	Quite distinct.
0·005 ,,	0·1 ,,	0·1 ,,	,,
0·001 ,,	0·1 ,,	0·1 ,,	,,
0·0005 ,,	0·1 ,,	0·1 ,,	Distinct.
0·0002 ,,	0·1 ,,	0·1 ,,	Faint.
0·0001 ,,	0·1 ,,	0·1 ,,	Very faint.

TABLE II.

Concentration of $K_4Fe(CN)_6$.	Concentration of $K_3Fe(CN)_6$.	Concentration of KCNS.	Reaction for $K_3Fe(CN)_6$.
0·1 gm.	0·001 gm.	0·1 gm.	Distinct.
0·1 ,,	0·0005 ,,	0·1 ,,	,,
0·1 ,,	0·0002 ,,	0·1 ,,	,,
0·1 ,,	0·0001 ,,	0·1 ,,	,,

TABLE III.

Concentration of $K_4Fe(CN)_6$.	Concentration of $K_3Fe(CN)_6$.	Concentration of KCNS.	Reaction for KCNS.
0·1 gm.	0·1 gm.	0·001 gm.	Quite sharp.
0·1 ,,	0·1 ,,	0·0005 ,,	,,
0·1 ,,	0·1 ,,	0·0002 ,,	Faint.
0·1 ,,	0·1 ,,	0·0001 ,,	,,

When the quantity of thiocyanate is very small, the green colour of the nickel salt tends to interfere with the red coloration produced by ferric chloride and potassium thiocyanate. So in Table III, with 0·0002 and 0·0001 gm. of thiocyanate, a faint coloration was obtained. This difficulty can however be removed by separating the nickel with a little sodium hydroxide solution before adding ferric chloride to it.

TABLE IV.

Concentration of $K_4Fe(CN)_6$.	Concentration of $K_3Fe(CN)_6$.	Concentration of KCNS.	Reaction for $K_4Fe(CN)_6$, $K_3Fe(CN)_6$. KCNS.
0·01 gm.	0·01 gm.	0·01 gm.	Sharp reactions for all the three.
0·005 ,,	0·005 ,,	0·005 ,,	,,
0·001 ,,	0·001 ,,	0·001 ,,	,,
0·0005 ,,	0·0005 ,,	0·0005 ,,	,,

Ferricyanide can also be detected after the separation of ferrocyanide, by reducing it with some reducing agent, such as alkaline hydrazine sulphate or hydroxylamine hydrochloride and then precipitating it again as ferrocyanide.

The solution, after the separation of ferrocyanide with an excess of cerous nitrate, was reduced with an ammoniacal solution of hydrazine sulphate or hydroxylamine hydrochloride until it became almost perfectly colourless.* A white precipitate of cerous ferrocyanide was at once formed by the excess of cerous nitrate already present in

* Reduction can also be carried out by making the solution strongly alkaline with caustic soda or potash and then adding ferrous sulphate or better, manganous or cobaltous chloride (" Cyanogen Compounds," H. E. Williams).

the solution. Some more cerous nitrate was added so as to make the precipitation complete. This was filtered, washed and analysed as usual. Cerous ferrocyanide formed at this stage may contain a little cerous hydroxide on account of the presence of free ammonia, but it does no harm. Thiocyanate was detected in the filtrate, after acidifying it with hydrochloric acid, with a few drops of ferric chloride.

A few results are given below:—

Concentration of $K_4Fe(CN)_6$.	Concentration of $K_3Fe(CN)_6$.	Concentration of KCNS.	Reaction for $K_3Fe(CN)_6$ and KCNS.
0·1 gm.	0·01 gm.	0·01 gm.	Quite sharp.
0·1 ,,	0·001 ,,	0·001 ,,	,, ,,
0·1 ,,	0·0005 ,,	0·0005 ,,	,, ,,

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Naphthalene Ring and Sugden's Parachors. Part III.

By S. S. Bhatnagar and Balwant Singh.

Macleod (*Trans. Farad. Soc.*, 1923, **19**, 38) has shown that over a wide range of substances the relationship given below holds:

$$y = C(D-d)^4$$

where y is the surface-tension in dynes/cm., D and d, the densities of the substance and its vapour respectively, and C, the Macleod's constant. From this it follows that $C = y/(D-d)^4$.

If the fourth root of the Macleod constant be multiplied by the molecular weight (M), the following expression is obtained: –

$$P = \sqrt[4]{C} \times M = \frac{M}{(D-d)} \times y^{\frac{1}{4}} \qquad \ldots \quad (1)$$

The quantity $M/(D-d)$ has the dimensions of volume, and at low temperatures, where d becomes very small, this represents, in fact, the molecular volume. The quantity (P) has been named as the "Parachor" by Sugden (*J. Chem. Soc.*, 1924, **125**, 1177). He has shown that this molecular parachor is an additive product of its atomic and structural parachors, the values for most of which have been obtained by him.

In a previous paper (*J. Chim. phys.*, 1928, **25**, 21) the authors calculated the value for the parachor of the naphthalene structure as 9·3 by the formula $23{\cdot}2x/n$ (Sugden and Wilkins, *J. Chem. Soc.*, 1927, **131**, 139), where x represents the number of latent valencies and n the number of octets in the structure.

In a private communication Sugden suggested that the value for the parachor of the naphthalene ring might be best represented if we take it to be as composed of two separate six-membered rings. On this viewpoint the value of the naphthalene ring would be $2 \times 6{\cdot}1 = 12{\cdot}2$, where 6·1 is the value of the parachor for the benzene ring.

The present investigation was undertaken to test the validity of Sugden's suggestion on data previously described and from the values of surface tension of naphthalene compounds now determined by the authors.

Experimental.

The determination of the parachor involves the measurement of surface tension and density at a series of temperatures ; the parachor is then calculated by the formula (1). For the substances described below, d was calculated by the method of Sugden (*J. Chem. Soc.*, 1925, **129**, 1525) and found to be very small at the temperature of observation and has been neglected. Densities were determined with a U-shaped pyknometer (Sugden, *J. Chem. Soc.*, 1924, **125**, 1167) and surface tension by the maximum bubble pressure method with an apparatus previously described by the authors (*loc. cit.*). The results are given in Table I.

Table I.

Substance.	Temperature.	Density, gms./c.c.	Surface tension, dynes/cm.	Parachor (P) obs.
Naphthalene.	80·1°	0·9765	32·26	312·5
Acenaphthene.	128·6°	1·0020	31·36	364·1
	178·7°	0·9610	26·60	364·2
α-Chloro-naphthalene.	20°	1·1706	41·80	353·0
α-Bromo-naphthalene.	13·6°	1·488	45·97	362·3
	33·4°	1·470	43·96	362·6
	50·0°	1·454	42·13	362·6
	83·5°	1·425	38·92	362·8
				Mean = 362·6
α-Naphthol.	100·5°	1·103	38·88	326·2
	116·8°	1·090	37·16	326·4
	134·7°	1·076	35·51	327·0
				Mean = 326·5
β-Naphthol.	130·2°	1·078	36·45	328·3
	144·5°	1·067	35·14	328·6
	161·0°	1·055	33·70	329·0
				Mean = 328·6
α-Naphthylamine.	54·3°	1·100	47·25	341·0
	67·5°	1·090	45·81	341·5
	81·4°	1·079	44·16	341·8
	96·0°	1·068	42·52	342·2
				Mean = 341·6
β-Naphthylamine.	115·8°	1·049	39·29	341·5
	130·2°	1·039	37·91	341·8
	142·0°	1·031	36·87	342·0
				Mean = 341·8

The values of surface tension for naphthalene, acenaphthene and α-chloronaphthalene are taken from the following papers: –

1. Naphthalene (Bhatnagar and Singh, *J. Chim. phys.*, 1928, **25**, 21).

2. Acenaphthene (Dutoit and Friedrich, *Arch. Sci. phys. nat.*, 1900, **9**, 105).

3. α-Chloro-naphthalene (Harkins and Feldman, *J. Amer. Chem. Soc.*, 1922, **44**, 2665).

The naphthylamines were distilled and their surface tension determined in an atmosphere of nitrogen.

The values of the parachors for the above substances are calculated from the values of the various atomic and structural constants of Sugden (*J. Chem. Soc.*, 1924, **125**, 1187, and subsequent papers) assigning 12·2 and 9·3 as the value of the parachor for the naphthalene ring, where 12·2 is the value suggested privately by Sugden on the concept that the value for the ring constant is twice that found for the benzene ring, and 9·3 is the value calculated by the authors (*loc. cit.*). The value for OH group is taken from a previous paper of the authors (*loc. cit.*).

The values of the parachor $(P)_{cal.\ 12\cdot2}$ and $(P)_{cal.\ 9\cdot3}$ calculated, taking 12·2 and 9·3 respectively as the value for the ring constant, are compared with the vaues of the parachors $(P)_{obs.}$ obtained from the surface tension data in Table II.

TABLE II.

Substance.	Parachor observed. $(P)_{obs.}$	Parachor $(P)_{cal.\ 12\cdot2}$	Parachor $(P)_{cal.\ 9\cdot3.}$
Naphthalene.	312·5	313·0	310·1
Acenaphthene.	364·2	365·3	362·4
α-Chloro-naphthalene.	353·0	350·2	347·3
α-Bromo-naphthalene.	362·6	363·9	361·0
α-Naphthol.	326·5	326·3	323·4
β-Naphthol.	328·6	326·3	323·4
α-Naphthylamine.	341·6	342·6	339·7
β-Naphthylamine.	341·8	342·6	339·7

From the above table it is evident that the values of the parachors calculated with 12·2 as the ring constant for naphthalene

are in better agreement with the observed parachors than the values calculated with 9·3 as the ring-constant.

The ring-constant for naphthalene, therefore, is the sum of two six-membered ring-constants ($2 \times 6{\cdot}1 = 12{\cdot}2$). This view is also supported by the work on decahydro-naphthalenes (Vogel, *J. Chem. Soc.*, 1928, **133**, 2017) in which case the value for the ring-constant is practically twice that found for the *cyclo*hexane ring.

Summary.

1. Surface tensions and densities of α-bromonaphthalene, α-naphthol, β-naphthol, α-naphthylamine and β-naphthylamine have been determined at various temperatures.

2. Parachors for these substances have been calculated from the observed data as well as from the values of atomic and structural parachors.

3. The value of the parachor for naphthalene ring has been found to be 12·2.

In conclusion the authors wish to express their indebtedness to Dr. S. Sugden for his valuable suggestion.

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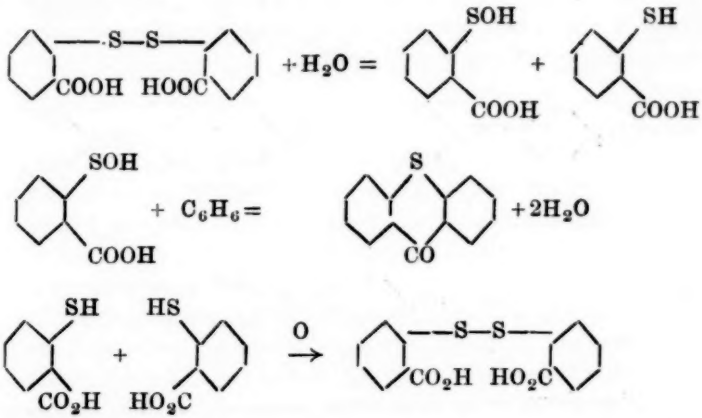
Studies in the Condensation of Di-*ortho*-thiobenzoic Acid with Aromatic Hydroxy Compounds.

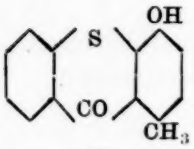
By Rajendra Nath Sen and Suresh Chandra Sen-Gupta.

The interaction between di-*o*-thiobenzoic acid and simple aromatic compounds such as benzene, xylene, *p*-chloro-phenol, in presence of concentrated sulphuric acid was studied by Prescott and Smiles (*J. Chem. Soc.*, 1911, **99**, 640) and by Marsden and Smiles (*J. Chem. Soc.*, 1911, **99**, 1353), who observed that the di-*o*-thiobenzoic acid, in presence of sulphuric acid and a simple aromatic compound, splits up into a mercaptan and a sulphoxylic acid; the latter substance then condenses with aromatic compounds to form thio-xanthones, and "the remaining mercaptan is reoxidised by the sulphuric acid to the original disulphide. Thus sulphur dioxide is continually liberated during the reaction, and the rupture of the disulphide continues."



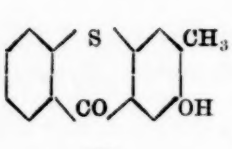
In the present work, the condensations of di-*o*-thiobenzoic acid specially with aromatic hydroxy compounds have been investigated with a view to prepare and study thioxanthone dyes. In this connection several interesting observations have been made regarding the reaction and the tinctorial character of the resulting products.

Thus the three cresols condense with the acid in presence of sulphuric acid at 95°—100°. The products obtained are the three methylhydroxy-thioxanthones.



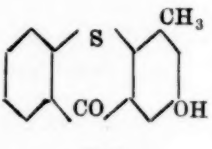
(I).

1-Methyl-4-hydroxy-thioxanthone.



(II).

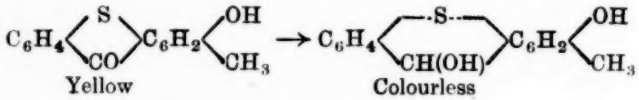
3-Methyl-2-hydroxy-thioxanthone.



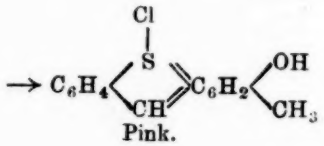
(III).

4-Methyl-2-hydroxy-thioxanthone.

These three compounds readily dissolve in alkali hydroxide solution, from which they are easily separated by saturating the solution with carbon dioxide, and they all form monobenzoyl derivatives. The introduction of one auxochrome group (OH) into the simple thioxanthone chromogen brings out the tinctorial properties of the compounds which are all yellow, and dye wool light yellow shades. The behaviour of these compounds on reduction is quite interesting. Thus when reduced with zinc dust in caustic soda solution, the reduction products, which are presumably xanthydrols, are colourless but on adding hydrochloric acid pink colour appears, which is probably due to salt formation with elimination of water and production of an *o*-quinonoid configuration.



Yellow Colourless



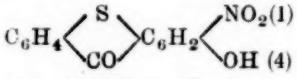
Pink.

p-Nitro-phenol is found to be far more reactive than the cresols and condenses with the di-thio-acid readily. This is due to the presence of nitro group in the nucleus. The product (IV) dissolves in alkali hydroxide solution from which it is not precipitated with carbon dioxide, which is due to the increased acidic property of the OH group in presence of a nitro group in the nucleus. The

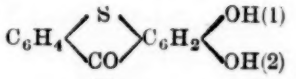
compound possesses a brownish black colour and the ammonium salt dyes wool in blackish brown shade from an acid bath.

The condensation products of the di-thio-acid with the di-hydroxy benzenes have offered a very interesting study.

Catechol condenses with the di-*o*-thio-benzoic acid producing 1:2-dihydroxy-thioxanthone (V). The compound is brown and dissolves in alkali hydroxide solution with crimson colour, from which carbon dioxide precipitates the compound.



(IV).



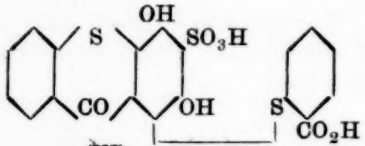
(V).

It has been given this constitution from analogy with alizarine. Like alizarine it possesses very marked polygenetic properties dyeing wool greenish black with iron mordant and beautiful chocolate shade with chromium mordant. Thus replacing one CO group in alizarin by sulphur, the polygenetic property of the dyestuff is not affected, although it is very remarkable that alumina mordanted cotton is dyed a yellow shade only.

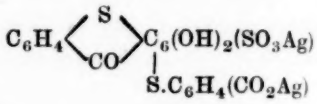
Resorcin also condenses with the acid at 95°—100°. The analyses of the product (VI) and its potassium and silver salts indicate the condensation of two molecules of sulphoxylic acid with one molecule of resorcinol, and also the sulphonation of the resulting product (the position of the sulphonic acid group being uncertain). The green condensation product gives a green solution in water and a red solution with alkalis. If CO_2 be passed into the red alkaline solution no precipitation takes place nor does the original green colour reappear; but on neutralising the solution with HCl, the green colour reappears and on adding excess of HCl the green compound separates out; this behaviour is in perfect agreement with the presence of carboxyl and sulphonic acid groups. Further the analysis of the potassium salt of the compound shows that a tetra-potassium salt is formed as expected. The presence of a carboxyl and a sulphonic acid group is also supported by the following observations.

When the red aqueous ammoniacal solution of the compound is dried on the water-bath, ammonia is given off and the dried mass thus obtained gives a pale reddish yellow solution much lighter than the original solution; and the silver salt obtained from this

ammonium salt shows on analysis that a di-silver salt (VII) has been formed, which is best accounted for by assuming that the ammonium groups replacing the hydrogen atoms of the hydroxyl groups have been eliminated as ammonia when heated,



(VI).



(VII).

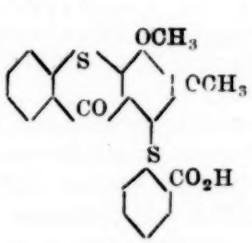
and that the ammonium groups replacing the H of the carboxyl and sulphonic acid groups only have been replaced by Ag. Again the silver salt obtained by adding silver nitrate solution directly to the aqueous solution of the compound shows, on analysis, that the same di-silver salt is formed, confirming the presence of two acid groups in the molecule. It may be noted that no lactone formation takes place in this compound though such a possibility exists. The colour of the compound is deep green and it dyes wool in green shade from an acid bath. This compound is readily soluble in water and alcohol, but another product, obtained by heating resorcin with the di-thio-acid in presence of sulphuric acid at 120°-130° for about one hour, is found to be quite insoluble in water and alcohol though it is green like the former compound. This product, however, has not been obtained in a sufficiently pure condition for analysis.

Now the *o*-dihydroxy-thioxanthone (V) is brown and *p*-dihydroxy-thioxanthone (*J. Chem. Soc.*, 1911, **99**, 1535) is orange but the compound (VI) which is a derivative of *m*-dihydroxy-thioxanthone is green. It can hardly be expected that such a deep colour is due only to the difference in position of the hydroxyl groups; it is probable that the colour is also influenced by the presence of the additional group—$S.C_6H_4.CO_2H$. In order to decide whether such a deep colour is consistent with the simple constitution attributed to the compound, resorcin dimethyl ether has been condensed with the acid, in which case possibility of lactone formation is excluded.

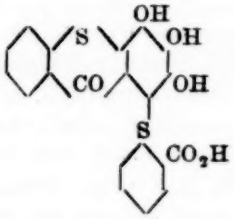
The condensation product (VIII) is also found to be bluish green. It is insoluble in water but soluble in alkali carbonate solution with a red colour and therefore contains a free carboxyl group. It is found, however, not to have been sulphonated and it gives a mono-potassium salt only. By replacing the two hydroxyl groups of the

compound (VI) by two methoxyl groups, the colour of the compound only changes from deep green to bluish green.

In order to study the effect of an additional hydroxyl group, pyrogallol is condensed with the di-thio-acid. The condensation takes place with two molecules of the sulphoxylic acid. The product (IX) is readily soluble in alkali carbonate solution indicating a free carboxyl group.

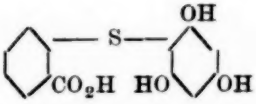


(VIII).

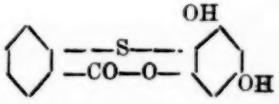


(IX).

When acetylated it gives a tri-acetyl derivative. The compound shows very marked polygenetic properties dyeing wool green with chromium mordant and greenish black with iron mordant. Aluminium mordanted cotton is dyed a brown shade. The condensation product of phloroglucinol with the di-thio-acid may be (X*a*) or the



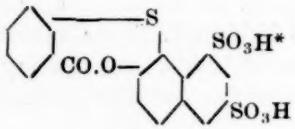
(X*a*).



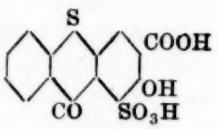
(X*b*).

reaction may proceed a step further producing a lactone (X*b*) (xanthone formation being not possible). The analysis supports the formula (X*b*). The compound dissolves in alkali hydroxide solution from which it is reprecipitated with HCl but not by CO_2, this being undoubtedly due to the scission of the lactone ring and formation of an alkali salt of the carboxyl group. The ammonium salt of the compouud dyes wool a light brownish shade from an acid bath. The product (XI) obtained by condensing β-naphthol with the acid is a disulphonic acid. In this compound the sulphur is attached to the

α-position and consequently, in this case also, lactone-ring formation takes place.



(XI)



(XII)

It gives a tetra-potassium salt, the lactone ring being broken up. The compound is greenish-black and dyes wool in a light brownish-yellow shade from an acid bath.

In order to prepare other mordant thio-xanthone dyes in this group, salicylic acid, 1:2:3- and 1:2:5-cresotinic acids have been condensed with the di-thio-acid. The condensation product (XII) with salicylic acid is obtained as a mono-sulphonic acid compound, which is brownish yellow, the position of the sulphonic acid group being uncertain.

Though it contains OH and COOH groups in *o*-position to each other, it does not, however, show polygenetic properties. It dyes both iron and chromium mordanted wool yellow shades with slight difference. The condensation products with cresotinic acids, however, show polygenetic properties by qualitative tests.

Experimental.

The di-*o*-thiobenzoic acid used in the condensations was prepared from anthranillic acid. Anthranillic acid (23 g.) was mixed with hydrochloric acid (*d* 1·19, 48 c.c. and 100 c.c. water) and then diazotised by the addition of a conc. aqueous solution of sodium nitrite, (about 14 g.) keeping the temparature below 3°. The diazo-solution was then slowly run in with constant stirring into a solution containing sulphur (6·7 g.) and sodium sulphide (52 g.) in 58 c.c. of water to which 24 gm. of aqueous caustic soda (*d* 1·38) had been previously added. Throughout the operation the temperature was kept below +5° by the addition of ice. After a short

* The condensation product of β-naphthol-6:8-disulphonic acid with the di-thio-acid, obtained under similar conditions, exhibits properties similar to those of compound (XI) indicating the positions of the SO_3H groups. As however it was prepared only in a small quantity and not in a sufficiently pure condition, the percentage of sulphur was a little too low.

time the temperature gradually rose up due to the formation of di-*o*-thiobenzoic acid. After two hours, the clear solution of the sodium salt of the acid was filtered from the unacted upon sulphur which separated out. Hydrochloric acid was then added to the solution until it was acid to congo red paper, and the precipitated di-thio-acid was filtered and thoroughly washed.

1-*Methyl*-4-*hydroxythioxanthone* (I).—The di-thio-acid (5 g., 1 mol.) and *p*-cresol (5 g., 2 mols.) were mixed with sulphuric acid (10 c.c., *d* 1·84). The reaction started at the ordinary temperature but was completed by heating the mixture on boiling water-bath for about 8 hours. Pounded ice was then added to the mixture and the yellow mass was thoroughly washed with cold water to remove sulphuric acid. It was then dissolved in hot caustic soda solution, filtered and the solution was saturated with carbon dioxide, when the methyl-hydroxy-thioxanthone separated out. It was then filtered, thoroughly washed with water and, after drying, crystallised from hot (50°-60°) absolute alcohol as yellow, shinning, silky, microcrystals, m.p. 234° with decomposition. It is soluble in hot alcohol, glacial acetic acid, pyridine, and slightly soluble in chloroform. The *sodium salt* of the compound crystallises from water in orange yellow needles. The *ammonium salt* dyes wool a greenish yellow shade from an acid bath. (Found: S, 13·2 ; C, 69·3 ; H, 4·2. $C_{14}H_{10}O_2S$ requires S, 13·2 ; C, 69·4 ; H, 4·1 per cent.)

Benzoyl derivative.—The benzoyl derivative was prepared in the cold. It was crystallised from a mixture of alcohol and chloroform as yellow microcrystalline powder melting at 176°-177°. It readily dissolves in chloroform but is insoluble in alcohol. (Found: S, 9·0. $C_{21}H_{14}O_3S$ requires S, 9·2 per cent.)

3-*Methyl*-2-*hydroxythioxanthone* (II).—The condensation was carried out as in the case of *p*-cresol, and the product purified similarly. It was obtained as a yellow microcrystalline powder melting at 210°-212°. It is soluble in absolute alcohol, glacial acetic acid and pyridine. Its *ammonium salt* dyes wool greenish yellow shade from an acid bath. (Found: S, 13·25; C, 69·19 ; H, 4·2. $C_{14}H_{10}O_2S$ requires S, 13·2 ; C, 69·19 ; H, 4·1 per cent.)

The *benzoyl derivative* was prepared and purified as in the case the benzoyl derivative of 1-methyl-4-hydroxy-thioxanthone. It was obtained as pale yellow crystalline powder melting at 129°-130°. (Found: S, 9·3. $C_{21}H_{14}O_3S$ requires S, 9·2 per cent.)

4-Methyl-2-hydroxythioxanthone (III).—The condensation was carried on as in the case of *p*-cresol. The reaction being completed, ice water was added to the mixture and the soft pasty mass hardened on keeping overnight. It was then purified as in the case of 1-methyl-4-hydroxy-thioxanthone. It crystallises from absolute alcohol as yellow microcrystalline powder which begins to shrink on heating above 170° and melts with decomposition at 190°. The *ammonium salt* dyes wool in a greenish yellow shade from an acid bath. It is soluble in alcohol, glacial acetic acid and pyridine. (Found: S, 13·3 ; C, 69·2 ; H, 4·4. $C_{14}H_{10}O_2S$ requires S, 13·2 ; C, 69·4 ; H, 4·1 per cent.)

1-Nitro-4-hydroxythioxanthone (IV).—Equal amounts of *p*-nitrophenol and the di-thio-acid were mixed with conc. sulphuric acid when much heat was evolved. The mixture was heated on the water-bath at 80° for about 2 hours. The product was thoroughly washed with cold water, dissolved in caustic soda solution, filtered and precipitated with hydrochloric acid. It was then dried and extracted with pyridine. On pouring the pyridine solution in alcohol, the compound separated out in microcrystalline form. It does not melt on heating to 280°. The compound is brownish; the *ammonium salt* dyes wool a blackish brown shade from an acid bath. (Found: S, 11·9 ; C, 56·8 ; H, 2·7. $C_{13}H_7O_4NS$ requires S, 11·7 ; C, 57·1 ; H, 2·5 per cent.)

1:2-Dihydroxy-thioxanthone (V) was prepared and purified as usual. It was necessary to recrystallise the compound several times from absolute alcohol in order to get it pure. It is a brown crystalline powder melting at 245°-248° with decomposition. It dyes wool a beautiful chocolate shade with chromium mordant and greenish black with iron mordant; alumina mordanted cotton is also dyed a bright yellow shade. It is soluble in alcohol and pyridine. (Found: S, 13·5 ; C, 63·5 ; H, 3·6. $C_{13}H_8O_3S$ requires S, 13·1 ; C, 63·9 ; H, 3·3 per cent.)

Condensation of Di-o-thiobenzoic acid with Resorcin.—Resorcin (3 g.), the di-thio-acid (3 g.) and concentrated sulphuric acid (8 c.c.) were heated on boiling water-bath for 8 hours. The pink mass, on adding water, changed to green. The product being soluble in water, was poured in dilute hydrochloric acid (1 : 1) and set aside overnight. The precipitate was thoroughly washed with dilute HCl to remove sulphuric acid and was dissolved in the least amount of hot water, filtered and a little strong HCl was added to the solution

when the product gradually separated out. It was then filtered and washed thoroughly with dilute HCl. The product was then dried and extracted with hot alcohol in which it dissolved readily. A few drops of hydrochloric acid were added to the alcoholic solution and in a short time the product separated out. It was then filtered, thoroughly washed with dilute HCl to remove traces of sulphuric acid and was dried in an air-bath at 110°-120°, as it tenaciously retained some water. The compound does not melt when heated even to 280°. It dyes wool green from an acid bath. It is soluble in alcohol and pyridine. (Found: S, 20·2 ; C, 50·1 ; H, 2·7. $C_{20}H_{12}O_8S_3$ requires S, 20·1 ; C, 50·4 ; H, 2·5 per cent.)

The *potassium salt* of the above compound was prepared by adding 0·5 gm. of the substance to a solution of about 0·3 gm. of pure caustic potash and the filtered solution evaporated to dryness on the water-bath. The dried salt was quickly powdered and thoroughly washed with absolute alcohol to remove any excess of caustic potash. The potassium salt was obtained as red powder. (Found: K, 24·3. $C_{20}H_8O_8S_3K_4$ requires K, 24·8 per cent.)

The potassium salt obtained by adding alcoholic potash to the alcohol solution of the compound gives a low percentage of potassium, which may be due to simultaneous separation of di- and tri-potassium salts.

Silver salt.—The compound was dissolved in aqueous ammonia, and evaporated to dryness on water-bath. The dried ammonium salt was dissolved in water and silver nitrate solution added when the silver salt separated out. (Found: Ag, 31·6. $C_{14}H_{10}O_8S_3Ag_2$ requires Ag, 31·3 per cent.)

Condensation of Di-o-thiobenzoic acid with Resorcin dimethyl-ether (VIII).—The condensation is carried out as described above. Ice-water is then added and the solid product washed with cold water. It is extracted with cold dilute sodium carbonate solution from which dilute HCl precipitates the compound. The process is repeated and the product washed with water. It is dried in an air-bath at 110°-120°. The compound is bluish green but its K-salt is red. It is insoluble in common organic solvents and does not melt on heating even to 280°. It dyes wool a light blue shade from sulphuric acid solution largely diluted with water. (Found: C, 61·7 ; H, 4·0 ; OMe, 14·0. $C_{22}H_{16}O_5S_2$ requires C, 62·2 ; H, 3·7 ; OMe, 14·6 per cent.)

The *K-salt* was prepared as in the case of the resorcin compound. (Found: K, 9·1. $C_{22}H_{15}O_5S_2K$ requires K, 8·6 per cent.)

Condensation of Di-o-thiobenzoic acid with Pyrogallol (IX).—The condensation is carried out as described before. The product is extracted with hot alcohol (absolute) from which it is obtained as a grey powder. It gives a red alkaline solution and is insoluble in water and in other common organic solvents except alcohol. It does not melt on heating even to 280°. It shows polygenetic properties dying wool green with chromium mordant and greenish black with iron mordant. It also dyes alumina mordanted cotton a brown shade. (Found: C, 57·9; H, 3·2. $C_{20}H_{12}O_6S_2$ requires C, 58·2 ; H, 2·9 per cent.)

The *acetyl derivative* is prepared by heating the compound with acetic anhydride and fused zinc chloride to 130° for 15 mins. It was crystallised from chloroform as a light brown powder. (Found: CH_3CO, 24·3. $C_{20}H_9O_6S_2(CH_3{\cdot}CO)_3$ requires $CH_3{\cdot}CO$, 23·9 per cent.)

Condensation of Di-o-thiobenzoic acid with Phloroglucinol.—The product was dissolved in caustic soda solution, precipitated with dilute HCl, filtered, washed, dried and crystallised from absolute alcohol. It was thus obtained as pinkish needles, melting at 166°. It is soluble in alcohol and pyridine. (Found: S, 12·2 ; C, 60·1 ; H, 3·0. $C_{13}H_8O_4S$ requires S, 12·2 ; C, 60·0 ; H, 3·0 per cent.)

The *ammonium salt* of the compound dyes wool in a light brownish red shade from an acid bath.

Condensation of Di-o-thiobenzoic acid with β-Naphthol.—The dithioacid (4 g.) and β-naphthol (4 g.) are mixed up with 15 c.c. of sulphuric acid and heated at 95°-100° for 15 hours. The mixture is poured in dilute hydrochloric acid (1 : 1) and allowed to stand overnight. The compound separates out and is filtered and washed with moderately dilute HCl, until free from sulphuric acid, and then dried in the steam-bath, extracted with hot absolute alcohol, from which the compound separates out on the addition of benzene as a greenish black powder. It does not melt when heated even to 280°. It is soluble in alcohol and pyridine.

It dyes wool a light brownish yellow shade from an acid bath. (Found: S, 22·4 ; C, 46·4 ; H, 2·3. $C_{17}H_{10}O_8S_3$ requires S, 21·9 ; C, 46·5 ; H, 2·4 per cent.)

The *tetra-potassium salt* was prepared by adding 1 gm. of the compound to a dilute solution of pure caustic potash containing about

0·4 gm. of KOH. The solution was evaporated to dryness, and the powdered salt washed thoroughly with absolute alcohol. (Found: K, 25·1. $C_{17}H_8O_9S_3K_4$ requires K, 25·6 per cent.)

Condensation of Di-o-thiobenzoic acid with Salicylic acid (XII).—The product was dried and then washed with a little chloroform to remove any free salicylic acid, and obtained as a brownish yellow powder from hot alcoholic solution. It does not melt on heating to 280°. It dyes wool a bright yellow shade with iron and chromium mordant producing only slight difference in shade. It is soluble in alcohol and pyridine. (Found: S, 18·4; C, 47·8; H, 2·4. $C_{14}H_8O_7S_2$ requires S, 18·1 ; C, 47·7 ; H, 2·2 per cent.).

Condensation of Di-o-thiobenzoic acid with 1:2 : 3- *and* 1: 2: 5-*Cresotinic acids*.—The di-thio-acid (1 mol.) and cresotinic acid (2 mols.) were taken.

The product from 1:2:3-cresotinic acid dyes iron mordanted wool brownish red shade and chromium mordanted wool a pinkish shade.

The compound from 1:2:5-cresotinic acid dyes chromium mordanted wool yellowish green shade and iron mordanted wool a brown shade.

N.B.—Sulphur in all the compounds has been estimated by fusion with sodium peroxide as Carius' method was found not to be very suitable.

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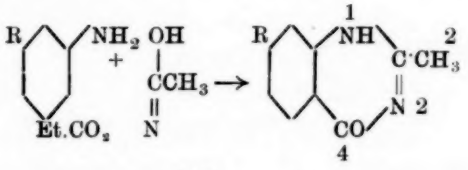
Received December 13, 1928.

A New Synthesis of Quinazolines. Part I.

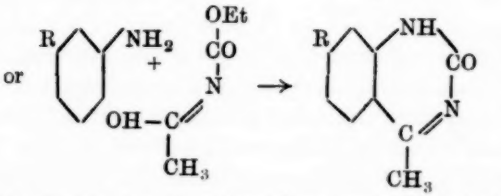
By Tarapada Bhattacharyya, Prafulla Kumar Bose and Jnanendra Nath Rây.

Phosphoric oxide induces the reaction between ethyl acetoacetate and phenols to give γ-pyrones (*cf.* Petschek and Simonis, *Ber.*, 1913, **46**, 2014). It suggested to the present authors that acetyl urethane $CH_3{\cdot}CO{\cdot}NHCOOC_2H_5$ which presents a unique similarity to acetoacetic ester, should also condense with amines under the influence of phosphoric oxide to give oxyquinazolines (I) or the isomeric substance (II).



(I)

or



(II)

For the preparation of quinazolines various methods have been employed (*cf.* Anschutz, Schmidt and Greiffenberg, *Ber.*, 1902, **35**, 3480; also Bogert and collaborators, *J. Amer. Chem. Soc.*, 1905, **27**, 649, 1305, 1327 ; 1906, **28**, 94, 207, 884, 1449; *cf.* also Bischler and Lang, *Ber.*, 1895, **28**, 282; Niementowski, *J. pr. Chem.*, 1895, (*ii*), **51**, 546; *Ber.*, 1896, **29**, 1360; *Annalen*, 1877, **184**, 349; *Ber.*, 1893, **26**, 1350, etc.) none of which has the advantage over the one proposed above.

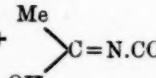
An isolated attempt to condense amines with acetyl urethane is recorded by Young (*J. Chem. Soc.*, 1898, **73**, 361). This investigator attempted to condense ammonia and amines with acetyl urethane without any condensing agent and was only able to isolate phenyl acetyl carbamide and a trace of acetanilide in the condensation with aniline. Therefore it was deemed advisable to study this reaction with amines under the influence of the condensing agent which one

of us successfully employed before in similar reactions (*cf.* Sen and Rây, *J. Chem. Soc.*, 1926, **129**, 646; De and Rây, *J. Indian Chem. Soc.*, 1927, **4**, 541).

The condition chosen for the reaction was very similar to that of De and Rây (*loc. cit.*). Two products were isolated, one crystallised out from the xylene employed as a diluent in the reaction, and another substance was obtained after neutralisation of the phosphoric acid sulution obtained by decomposing the reaction product with ice. This latter substance was basic and the non-basic product from xylene was found to be a carbamide derivative. The latter reaction can take place either as—

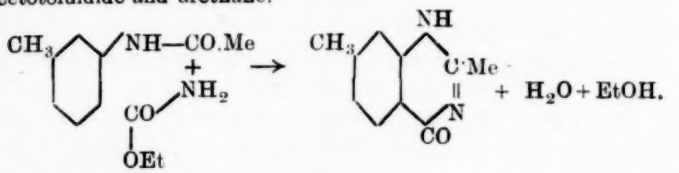
(1) $C_6H_5NH_2 + CH_3CO.NHCOEt = C_6H_5NH{\cdot}CO{\cdot}NH{\cdot}CO.CH_3$ (III)

+ Et OH, to give a carbamide,

or (2) $C_6H_5NH_2 +$  $= C_6H_5NH.CMe{=}N.COOEt$ (IV) $+ H_2O$.

to give an amidine.

Both products are formed but IV is distinctly basic in character and also unstable. Using a large excess of phosphoric oxide quinazolines are isolated from *m*-toluidine and *m*-anisidine. But the quinazolines may have either the structure I or II as the isolation of intermediates III and IV strongly suggests. To ascertain whether the quinazolines should be formulated as I or II, we condensed *m*-acetotoluidide and urethane.

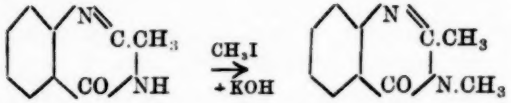


In the above reaction, the product can only be a 4-oxyquinazoline and we found that this product was identical with that we obtained from acetyl urethane and *m*-toluidine. Therefore we concluded that the quinazolines were really 4-oxy compounds instead of the isomeric 2-oxy derivatives, and in this reaction the course is parallel to that depicted by Simonis (*loc. cit.*) in his γ-chromone synthesis.

Having found the optimum conditions for the reaction we have reacted a number of acylamines with urethane and obtained the

corresponding quinazolines. The procedure adopted has essentially been the same as that of De and Rây in their investigation of the alleged constitution of vasicine (*loc. cit.*)

These quinazolines easily methylate with methyl iodide and potassium hydroxide in alcohol and we agree with Bogert and Seil (*loc. cit.*) in assigning a N-CH_3 structure to the methylated derivatives.



This is also in harmony with some further work that has since been done by one of us.

Experimental.

Condensation of Acetyl urethane with m-*Toluidine*: *Formation of* (a) *Acetyl* m-*tolyl carbamide* $CH_3.C_6H_4.NHCO.NHCO.CH_3$ *and*

(b) 2:7-*Dimethyl-4-oxyquinazoline* (Formula I, R=CH_3).

(*a*) Acetyl urethane (8 g.), *m*-toluidine (6 g.) and dry xylene (25 c c.) were gradually treated with phosphoric oxide (10-12 g.) with stirring at 125°-135° for 3 hours. Xylene was decanted off from the sticky product and furnished a crystalline substance on cooling. This was recrystallised from alcohol, m. p. 123° (yield 3·5 gm.). (Found: N, 14·56. $C_{10}H_{12}O_2N_2$ requires N, 14·58 per cent.)

(*b*) The above experiment was repeated with 35 gms. of phosphoric oxide. The xylene solution furnished almost nothing. The sticky mass left in the vessel was decomposed with ice water and filtered from a little undissoved impurity. The aqueous solution was neutralised with aqueous sodium hydroxide till the solution remained only slightly acidic. A voluminous mass of a colourless substance separated which was collected and purified by recrystallisation from hot alcohol (twice); m. p. 244°. (Found: N, 16·01. $C_{10}H_{10}ON_2$ requires N, 16·09 per cent.) This substance did not depress the m. p. of the product obtained from acetyl *m*-toluidide and urethane and is obviously (*b*) of the title of this section.

Condensation of m-*Anisidine with Acetyl urethane*: *Preparation of* (c) m-*Methoxyphenyl acetyl carbamide and* (d) 2-*Methyl-7-methoxy-4-oxyquinazoline* (Formula I, R=OCH_3).

(*c*) An intimate mixture of urethane (7 g.), *m*-anisidine (5 g.) and phosphoric oxide (10 g.) in xylene (25 c.c.) was heated as in the previous experiment, when from the cold xylene solution, long colourless needles of (c) separated out; m.p. 200°, after recrystallisation from spirit. (Found : N, 13·27. $C_{10}H_{12}O_3N_2$ requires N, 13·46 per cent.)

(*d*) In the above experiment when 25 gms. of phosphoric oxide were used, the aqueous solution, obtained after decomposition of the product with crushed ice, gave on neutralisation a substance which melted at 257° after repeated crystallisations from dilute alcohol. (Found: N, 14·84. $C_{10}H_{10}O_2N_2$ requires N, 14·73 per cent.)

Condensation of Acetyl Urethane and Aniline : Formation of (e) *Acetyl Phenyl Carbamide and* (f) *Compound* (IV).—(*e*) Using a mixture of acetyl urethane (7 g.), aniline (5 g.), phosphoric oxide (10 g.) and xylene (20 c.c.), we obtained in the usual manner, from the xylene solution compound (*e*). Crystallised from alcohol; m.p. 183° (*cf.* Walther and Wlodkowski, *J. pr. Chem.*, 1899, (*ii*), **59** 266, who give 183-184°). (Found: N, 15·73. $C_9H_{10}O_2N_2$ requires N, 15·92 per cent.)

(*f*) The reaction product, after xylene had been decanted off in the above experiment, was dissolved in water, the aqueous solution was cooled in ice and basified. The separated solid crystallised from alcohol. (Found: N, 13·51. $C_{11}H_{14}O_2N_2$ requires N, 13·59 per cent.)

Condensation of Acetyl Ureathane with o-*Toluidine : Formation of Acetyl* o-*tolylurea.*—When acetyl urethane (7 g.), *o*-toluidine (5 g.), phosphoric oxide (12 g.) and xylene (20 c.c.) were heated at 130°-140° for 3 hours, from the decanted xylene solution was isolated the above compound. It was recrystallised from alcohol in slender needles, m.p. 166°. Walther and Wlodkowski (*loc. cit.*) gives m.p. 168°. (Found: N,14·62. Calc. N, 14·58 per cent.) No quinazoline could be isolated in this case in a pure state. Similarly when the above condensation was done with (*i*) *m*-asym-xylidine, (*ii*) *o*-phenetidine, (*iii*) *o*-anisidine, carbamides were isolated but not the amidines or quinazolines.

(*i*) The acetyl carbamide from *m*-asym.-xylidine, m.p. 194°. (Found: N, 13·37. Calc. N, 13·59 per cent.).

(*ii*) The acetyl carbamide from *o*-phenetidine was *m*-ethoxyphenyl acetyl carbamide, m.p. 203°. (Found: N, 12·33. Calc. N, 12·61 per cent.)

(*iii*) *o*-Methoxyphenyl acetyl carbamide from *o*-anisidine, m.p. 197°. (Found: N, 13·21. Calc. N, 13·46 per cent.).

Condensation of Acetanilide with Urethane: Formation of 2-Methyl-4-oxyquinazoline.—Acetanilide (9 g.), urethane (8 g.), was thoroughly ground together, heated with xylene (30 c.c.), and phosphoric oxide (35 g.) was gradually introduced into the mixture kept boiling at 145°-150° (bath temperature) for 6 hours. The product was cooled and water introduced with care. The aqueous solution, well freed from the xylene layer, was further cooled and treated with a strong solution of sodium hydroxide till the resulting solution was only slightly acidic. The separated precipitate, well washed with water, was crystallised from hot alcohol, m.p. 231° (yield, 2·5 g.) (Found: C, 67·05; H, 5·6; N, 17·14. $C_9H_8ON_2$ requires C, 67·50; H, 5·0; N, 17·50 per cent.) Bogert and Gotthelf (*J. Amer. Chem. Soc.*, 1900, **22**, 522) give the m.p. 232-233°.

2:3-Dimethyl-4-oxyquinazoline.—The above substance (0·8 g.) m.p. 231° was dissolved in 10 c.c. of 2·8 per cent. solution of sodium hydroxide in methyl alcohol and refluxed with 0·8 c.c. of methyl iodide for three hours. On evaporation and washing the residue with dilute alkali and water, a substance was obtained which crystallised in fine long needles, m.p. 112°-113°: Bogert and Gotthelf (*loc.cit.*) give 110°-111°. (Found: N, 15·72. Calc. N, 16·08 per cent.)

Condensation of m-Acetotoluidide with Urethane: Formation of 2:7-Dimethyl-4-oxyquinazoline.—*m*-Acetotoluidide (8 g.), urethane (6 g.), phosphoric oxide (35 g.) and xylene (25 c.c.) were heated at 140°-150° (bath temperature) for 6 hours. The product after decomposition with water was isolated as usual from the aqueous solution by neutralisation and was crystallised from dilute alcohol (yield, 2 g.). (Found: N, 16·01. $C_{10}H_{10}ON_2$ requires N, 16·09 per cent.) The substance melted alone, or when mixed with the product from *m*-toluidine and acetyl urethane, at 244°.

Condensation of p-Acetotoluidide with Urethane: Formation of 2:6-Dimethyl-4-oxyquinazoline.—*p*-Acetotoluidide (8 g.), urethane (6 g.), phosphoric oxide (35 g.) and xylene (25 c.c.) were heated at 140°-150° for 6 hours. The product was isolated as usual and crystallised from dilute alcohol (twice). Yield 1·5 g.; m.p. 240°. The substance, like all the members of this series, dissolves in dilute acids and alkali (*cf.* Bischler and Muntemdam, *Ber.*, 1895, **28**, 729). (Found: N, 16·34. $C_{10}H_{10}ON_2$ requires N, 16·09 per cent.)

The *picrate* of the above quinazoline was prepared in alcoholic solution in the usual manner and crystallised from dilute alcohol. Yellowish crystals, m.p. 196-198°.

Condensation of Aceto-o-ioluidide with Urethane: Formation of 2:8-*Dimethyl*-4-*oxyquinazoline*.—Interaction of aceto-o-toluidide (9 g.), urethane (7 g.), phosphoric oxide (35 g.) in xylene (25 c.c.) at 140°-150° for 6 hours, furnished the substance and was isolated in the usual manner. The yield of the recrystallised product from dilute alcohol was 2 g.; m.p. 240°. The substance is very soluble in acids, alkali and alcohol. (Found: N, 15·72. $C_{10}H_{10}ON_2$ requires N, 16·09 per cent.). *Picrate*, m.p. 164°.

2:3:8-*Trimethyl*-4-*oxyquinazoline*.—One g. of the above quinazoline dissolved in 10 c.c. of 2·8% solution of potassium hydroxide in methyl alcohol was refluxed with 0·7 c.c. of methyl iodide for 3 hours. The residue after the evaporation of the solvent was washed with dilute alkali and water and crystallised from dilute alcohol in thick plates, m.p. 107°. The substance was now insoluble in alkali. (Found: N, 14·88. $C_{11}H_{12}ON_2$ requires N, 14·88 per cent.).

Condensation of Aceto-m-asym-*xylidide with Urethane: Formation of* 2:6:8-*Trimethyl*-4-*oxyquinazoline*.

Aceto-*m*-xylidide (8 g.), urethane (6 g.), phosphoric oxide (35 g.) in xylene (25 c.c.) where heated for 6 hours at 145-155°. The product after isolation by the usual method crystallised from hot absolute alcohol (yield, 3 g.), m.p. 266° (*cf.* Bamberger and Weiler, *J.pr. Chem.*, 1898, (*ii*) **58** 333 give m.p. 271°). (Found: N, 14·88. $C_{11}H_{12}ON_2$ requires N, 14·88 per cent.). It formed a *picrate*, m.p. 197°.

2:3:6:8-*Tetramethyl*-4-*quinazolone*.—2:6:8-Trimethylquinazolone gives, on methylation in dilute alkali solution with methyl iodide, the above compound, m.p. 146° after crystallisation from alcohol. (Found: N, 13·69. $C_{12}H_{14}ON_2$ requires N, 13·86 per cent.).

2:6:8-*Trimethyl*-3-*ethyl*-4-*quinazolone* was prepared similarly to the tetramethyl compound using ethyl iodide in the place of methyl iodide; m.p. 190°. (Found: N, 13·09. $C_{13}H_{16}ON_2$ requires N, 12·96 per cent.). The substance is soluble in acids but insoluble in alkalis.

Condensation of Aceto-p-*anisidide with Urethane: Formation of* 2-*Methyl*-6-*methoxy*-4 *oxyquinazoline*.

Aceto-*p*-anisidide (8 g.), urethane (6 g.), phosphoric oxide (35 g.) in xylene (25 c.c.) were heated for 6 hours at 140°-150°. The product was isolated in the usual manner. It crystallised from absolute alcohol in shining plates, m.p. 257° (yield, 3 g.). The substance is very easily soluble in acids and alkalis. (Found: N, 14·65. $C_{10}H_{10}O_2N_2$ requires

N, 14·73 per cent.). The *N*-methyl derivative of the compound, *i.e.*, 2:3-dimethyl-6-methoxy-4-quinazolone was prepared by methylation with methyl iodide in alkali; m.p. 131°. (Found: N, 13·57. $C_{11}H_{12}O_2N_2$ requires N, 13·72 per cent.).

Condensation of Aceto-o-anisidide with Urethane.

2-Methyl-8-methoxy-4-oxyquinazoline was prepared from aceto-*o*-anisidide (8 g.), urethane (7 g.), phosphoric oxide (35 g.) in xylene (25 c.c.) at 140°-150° for 5 hours. The product isolated in the usual manner was purified by crystallisation from alcohol, m.p. 243°; yield, 2 g. (Found: N, 14·55. $C_{10}H_{10}O_2N_2$ requires N, 14·73 per cent.).

Methylation in the usual manner furnished *2:3-dimethyl-8-methoxy-4-quinazolone.*

Condensation of Aceto-p-phenetidide with Urethane: *2-Methyl-6-ethoxy-4-oxyquinazoline*, melting at at 220°, was isolated in good yield from the above constituents after interaction in the usual manner. The substance, when crystallised from alcohol has a slight greenish tinge. (Found: C, 64·9; H, 6·07; N, 13·74. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·88 N, 13·72 per cent.). *2:3-Dimethyl-6-ethoxy-4-oxyquinazoline* was prepared by methylation of the compound, m.p. 220°. The substance crystallised in stout prisms with a slight yellowish tinge; m.p. 148° (Found: N, 12·94. $C_{12}H_{14}O_2N_2$ requires N, 12·84 per cent.).

Condensation of Aceto-o-phenetidide and Urethane: *Formation of 2-Methyl-3-ethoxy-4-oxyquinazoline.*

The above substance was prepared from aceto-*o*-phenetidide, urethane and phosphoric oxide. The reaction product was decomposed with water and the substance isolated from the aqueous solution in the usual manner. It crystallised from alcohol in slender needles, m.p. 225°. (Found: N, 13·57. $C_{11}H_{12}O_2N_2$ requires N, 13·72 per cent.)

Condensation of Aceto-α-naphthalide with Urethane: *Formation of 2-Methyl-7:8-benzo-4-oxyquinazoline.*

1·5 G. of the above substance was isolated in the usual manner from aceto-α-naphthalide (5 g.), urethane (5 g.), phosphoric oxide (30 g.) and xylene (20 c.c.) after heating at 150°-160° for 6 hours. The substance crystallises from alcohol in fibrous needles with a slight yellow tinge, m.p. 322°. It is easily soluble in pyridine and dilute alkali. (Found: N, 13·12. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.).

Condensation of Aceto-β-naphthalide with Urethane: Formation of 2-Methyl-5:6-benzo-4-oxyquinazoline.

Aceto-β-naphthalide (8 g.), urethane (8 g.) phosphoric oxide (35 g.) and xylene (25 c.c.) were used in this reaction. The product was isolated by adding water to the reaction mixture when the quinazoline came down. The substance is feebly basic and hence the acidic aqueous solution needs no neutralisation for its isolation. The substance was crystallised from pyridine (yield, 3 g.) in cottony needles, m.p. 295°. It is easily soluble in alkali. (Found: N, 13·20. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.).

The *N-methyl* derivative was prepared in the usual way and crystallised from dilute alcohol in needles, m.p. 156°. (Found: N, 12·37. $C_{14}H_{12}ON_2$ requires N, 12·50 per cent.).

Condensation of Benzanilide with Urethane: Formation of 2-Phenyl-4-oxyquinazoline.

Benzanilide (9 g.), urethane (10 g.) and phosphoric oxide (40 g.) in xylene (30 c.c.) when heated at 175°-190° (bath temperature) for 6 hours furnished the product after usual treatment. The yield was about 2 g. The substance crystallised from alcohol in pale greenish needles, m.p. 223° (*cf.* Bischler and Lang, *Ber.*, 1898, **29**, 279, who give m.p. 223-225°). (Found: N, 12·17. $C_{14}H_{10}ON_2$ requires N, 12·6 per cent.).

2-Phenyl-3-methyl-4-quinazolone was obtained by the methylation of the foregoing substance in the usual manner; m.p. 133°. (Korner, *J. pr. Chem.*, 1887, (*ii*) **36**, 155, gives 131°). (Found: N, 11·48. $C_{15}H_{12}ON_2$ requires N, 11·86 per cent.).

Condensation of Propionanilide with Urethane: Formation of 2-Ethyl-4-oxyquinazoline.

Propionanilide (9 g.), urethane (8 g.), and phosphoric oxide (35 g.) in xylene (25 c.c.) at a temperature of 140-150° gave nearly 4 g. of the above compound. The substance crystallises in fine long needles and melts at 227-228° (*cf.* Niementowski, *J. pr. Chem.*, 1895, (*ii*) **51**, 564, who gives 225°). (Found: C, 68·80; H, 6·00; N, 16·06. $C_{10}H_{10}ON_2$ requires C, 68·94; H, 5·75; N, 16·09 per cent.). Methylation in the usual manner gave *2-ethyl-3-methyl-4-quinazolone*; stout needles, m.p. 121° (*cf.* Gotthelf, *loc. cit.*, who gives m.p. 121°) (Found: N, 14·74. $C_{11}H_{12}ON_2$ requires N, 14·90 per cent.).

Condensation of Propion-o-toluidide with Urethane: Formation of 2-Ethyl-8-methyl-4-oxyquinazolone.

Propion-*o*-toluidide (7 g.), urethane (6 g.) and phosphoric oxide (30 g.) in xylene (20 c.c) were heated at 145°-155° for 5 hours. The yield was nearly 2·5 g. and the substance crystallised from alcohol in pale brownish needles, m.p. 215°. (Found: N, 14·67. $C_{11}H_{12}ON_2$ requires N, 14·89 per cent.).

Condensation of Propion-p toluidide with Urethane: Formation of 2-Ethyl-6-methyl-4-oxyquinazoline.

The proportion of the ingredients were as follows: Propion-*p*-toluidide (9 g.), urethane (8 g.), phosphoric oxide (35 g.) and xylene (25 c.c.). The reaction was carried out at 145°-155°. The yield was nearly 3·5 g. The substance crystallises in fine needles, m.p. 227°. (Found: N, 14·73. $C_{11}H_{12}ON_2$ requires N, 14·89 per cent.).

2-Ethyl-3:6-dimethyl-4-quinazolone was obtained by the methylation of the foregoing substance. It crystallised in plates from alcohol, m.p. 111°. (Found: N, 13·57. $C_{12}H_{14}ON_2$ requires N, 13·86 per cent.).

Our thanks are due to Sir P. C. Rây for his kind interest during this investigation.

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A Theory of Colour on the Basis of Molecular Strain. Part VII. The Effect of Polymembered Ring Formation.

By Amarendra Nath Dey and Sikhibhushan Dutt.

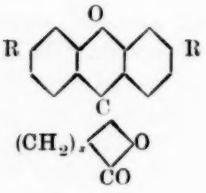
The present paper is the result of an investigation undertaken in connection with a theory of colour advanced by one of the present authors (Dutt, *J. Chem. Soc.*, 1926, **122**, 1171; *J. Indian Chem. Soc.*, 1927, **4**, 99), to find out the relative stability of a number of polymembered ring systems derived from the higher dibasic fatty acids, and to compare the depth of colour of a series of dyestuffs containing such rings.

According to the well known " strain theory " of Baeyer, cyclic compounds containing five and six members in the ring should be most stable, while the stability will gradually decrease as this limit is exceeded in either direction. With all the data that are at present available regarding the stability of the ring systems, it can be conclusively proved that though three and four membered rings are quite capable of existence, nevertheless they are unstable, and can be easily ruptured. But the same cannot be said with regard to cyclic compounds containing more than six members in the ring. For instance adipic anhydride, which contains a seven membered ring, has been proved to be a definite entity, while the cases of diphenic anhydride and suberone, containing seven membered rings, are particularly well known. By condensing diphenic anhydride with aromatic amino- and hydroxy-compounds, a series of dyestuffs belonging to the pyronine group has been obtained (Dutt, *J. Chem. Soc.*, 1923, **123**, 222), the colours of which are so light that there is no doubt about the fact that in these compounds the seven membered ring assumes the character of great stability.

About an eight membered ring, there is at present hardly any definite compound known containing such a ring, though from time to time various authors, in their publications, have assumed the existence of such ring formations. Borsche (*Ber.*, 1908, **31**, 1960)

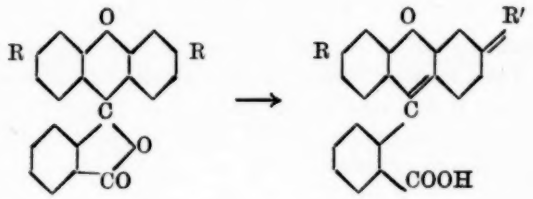
prepared from azelaic acid a ketone, which he considered to be *cyclo*octanone. Apart from this well known but isolated example, compounds containing eight or more members are very little known. All these data, somewhat scarce and conflicting though they are, clearly show that cyclic compounds containing more than six members are quite capable of formation and existence. If a chain of several carbon atoms is arranged in space, linked with one another by single linkage and with due conformation to their valency directions, it will be seen that instead of a straight line the carbon atoms get arranged in a spiral, with a tendency towards the formation of a complete cycle after every fifth carbon atom. Considered in that light it will be clearly seen that a five membered ring will be the most stable of all when the two ends of the spiral just complete a cycle, and the stability will gradually decrease until it reaches a minimum with the seventh member, when the two ends of the spiral are diametrically opposite to each other. After that the stability will again begin to increase with the eighth and ninth member since the ends of the spiral are tending to complete their second circle, and reach a culmination point again with the tenth member, when the ends are again near to each other.

In order to prove the truth of such a hypothesis, the following five acids, namely adipic, pimelic, suberic, azelaic and sebacic acids, have been condensed with resorcinol and *m*-diethylamidophenol with the formation of the corresponding fluoresceins and rhodamines. The intensity of their colour in solution is inversely proportional to the stability of their ring systems constituting their anhydrides as can be easily seen from the following configuration representing their general formula,



where R = OH or NEt_2, and x may be anything from 4 to 8. Such a compound on solution in alkali or acid will undergo fission of the lactone ring with the formation of a quinonoid structure and consequent

development of colour (Dutt and Thorpe, *J. Chem. Soc.*, 1924, **125**, 2524; Dutt, *J. Chem. Soc.*, 1926, **129**, 1132), thus:



where R′ = O or NEt_2Hal.

Therefore it will be clearly seen that the greater the stability of the lactone ring the less will be the colour development and *vice versa*. Actual data that have been obtained with regard to the intensity of colour of this series of compounds, show that they are in perfect accordance with the above supposition. The greatest development is seen in the case of compounds derived from adipic acid while the least is in the cases of azelaic and sebacic acids. Almost all these compounds, in general properties, colour and flourescence, resemble the corresponding derivatives of succinic and glutaric acids (Dutt and Thorpe, *loc. cit.*).

Experimental.

Resorcinol-adipein.—A mixture of adipic acid (5·5 g.), resorcinol (8·4 g.) and concentrated sulphuric acid (2 c.c.) was heated at 170-180° for about four hours. The melt was then dissolved in dilute ammonia and precipitated with dilute hydrochloric acid. The resultant precipitate was afterwards crystallised from acetic acid in brown needles, not melting below 286°. Unlike resorcinol-succinein the substance dissolves in alkalis with a dark red colour. The alkaline solutions are very unstable in presence of air. (Found: C, 61·4; H, 4·7. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1 per cent.).

m-*Diethylamidophenol-adipein.*—A mixture of *m*-diethylamidophenol (6·8 g.), adipic acid (2·9 g.) and a few drops of sulphuric acid was heated at 120-130° for about 20 hours, when the melt completely solidified and a little of it when tested gave a bright pink colour with dilute hydrochloric acid. The powdered melt was washed with water and dilute ammonia, dissolved in dilute hydrochloric

acid and reprecipitated with sodium carbonate. Finally it was crystallised from alcohol in pink needles sintering at 138°. (Found: N, 6·2. $C_{26}H_{34}N_2O_3$ requires N, 6·6 per cent.).

Resorcinol-pimelein.—This was prepared from pimelic acid and resorcinol in a manner similar to the corresponding compound of adipic acid. It was crystallised from dilute hydrochloric acid in glistening brown needles, melting at 164°. (Found: C, 69·6; H, 5·6. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5 per cent.).

Resorcinol-suberein.—Suberic acid (1·7 g.) and resorcinol (2·2 g.) were heated together with a few drops of concentrated sulphuric acid at 170° for about four hours, when the mixture completely solidified. The powdered product was washed with water and then crystallised from 5% hydrochloric acid in small glistening yellow needles, m. p. 140°. The substance dissolved in alkalis with a deep yellow colour and the solution on dilution showed an intense green flourescence. (Found: C, 70·0; H, 5·8. $C_{20}H_{20}O_5$ requires C, 70·5; H, 5·9 per cent.).

m-*Diethylamidophenol-suberein.*—This compound was prepared from *m*-diethylamidophenol and suberic acid in a similar way to the corresponding compound of adipic acid. It crystallised from alcohol in dark violet needles, m. p. 147°. (Found: N, 6·1. $C_{28}H_{38}O_3N_2$ requires N, 6·2 per cent.).

Resorcinol-azelaein.—This was prepared from azelaic acid and resorcinol in a similar way to resorcinol-adipein. It crystallised from glacial acetic acid in chocolate brown needles melting at 172°. (Found: C, 70·8; H, 6·0. $C_{21}H_{22}O_5$ requires C, 71·2; H, 6·04 per cent).

m-*Diethylamidophenol-azelaein.*—Prepared from *m*-diethylamidophenol and azelaic acid in a similar way to the corresponding compound from adipic acid. It could not be crystallised. It was obtained from alcohol as a violet-red powder dissolving in dilute hydrochloric acid with a brilliant pink colour, m.p. 126°. (Found: N, 6·0. $C_{29}H_{40}O_3N_2$ requires N, 6·03 per cent.).

Resorcinol-sebacein.—Prepared from sebacic acid and resorcinol in a similar way to resorcinol-adipein. It crystallised from dilute hydrochloric acid in glistening yellow needles, sintering at 166°. (Found: C, 71·22; H, 6·1. $C_{22}H_{24}O_5$ requires C, 71·74; H, 6·5 per cent.).

m-*Diethylamidophenol-sebacein*.—Prepared from *m*-diethylamidophenol and sebacic acid in a similar way to the corresponding adipic acid compound. It could not be crystallised. It was obtained from alcohol as a dark violet powder melting at 142°. (Found: N, 5·2. $C_{30}H_{42}N_2O_3$ requires N, 5·6 per cent.).

Absorption maxima of dyestuffs. (Figures indicate approximate wave-lengths).

Dyes derived from—	Rhodamine type.	Fluorescein type. In alcohol.	Fluorescein type. In KOH.
Adipic acid	5132	4910	5120
Pimelic ,,	—	4880	4930
Suberic ,,	5038	4865	4910
Azelaic ,,	5038	4823	4880
Sebacic ,,	5076	4830	4880

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Some Constituents of *Cæsalpinia Bonducella* Nut (Flem).

Part I. Bonducella Nut Oil.

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Cæsalpinia bonducella is a climbing shrub common all over Bengal, Bombay, Travancore and the Coromondal coast. It is known in Hindi as the Sagargota plant. The dry nut has an iron grey colour with a very hard and flexible rind which causes it to bounce like a ping-pong ball when it impinges on a hard surface. It is well-known in Indian homes especially among children. It has been recognised for a long time that the kernels of these nuts have anti-periodic and febrifuge properties. It is known abroad as the fever nut, and is thus administered in cases of intermittent fevers and cholic. The usual dose is form 5 to 30 grains. (Watt. "Dictionary of Economic Products of India," Vol. II, p. 4).

The present investigation was undertaken with a view to detect those substances in the nut which give it these characteristic properties. Before proceeding to the glucosides, we considered it advisable to examine the constituents of its oil, obtained from the petrol extracts of the dried and crushed kernels.

The nuts average 1·8 to 2 gm. in weight. The proportion of rind to kernel is 58·1 to 41·9. The percentage of oil yield, when extracted with petrol ether (60°—80°), on dried kernels was 20. The oil has a peculiar odour and a pale yellow colour. Lewkowistch ("Chemical Technology and Analysis of Oils, Fats and Waxes," 4th Ed., Vol. II, p. 192) mentions this as a semi-drying oil with a dark colour and peculiar odour. The petrol extracted kernels were tested for elements and gave positive tests for sulphur and nitrogen.

The nuts were pressed in a local *Ghana* and the oil obtained was clear and pale yellow in colour ; the quantity pressed being small, the percentage yield of oil, by this method, could not be calculated on account of wastage during the pressing operations.

The petrol ether extracted kernels were further extracted with absolute alcohol. On cooling the extract, a thick white precipitate

was obtained which was soluble in water (with frothing) and was identified as saponin. The alcohol was removed and the residue reduced Fehling's solution on hydrolysis with acid and was obviously a glucoside. This is the bitter principle which contains almost all the sulphur content of the *Bonducella* nut.

On treating the alcohol extracted kernel with distilled water, a further quantity of saponin was obtained. The baryta compound was precipitated, washed and decomposed with carbon dioxide, when saponin was obtained by concentrating the filtrate.

In another experiment the kernel, after the first petrol ether extraction, was further extracted with 2 % hydrochloric acid. This latter extract, on neutralisation with sodium carbonate solution, yielded a fluffy precipitate which was washed and preserved for further examination. It gave a feeble nitrogen test, but sulphur could not be detected. The fluffy precipitate was soluble in dilute hydrochloric acid and gave precipitates with picric acid and Froehde's reagent. The two dried precipitates, as well as the original substance, did not melt even at 295° but showed a slight charring only. This substance in dilute sulphuric acid solution decolorised potassium permanganate solution.

The work on the *Bonducella* oil was conducted on the usual lines. The constants of the oil and the fatty acids were determined. The saturated and unsaturated acids were separated by Twitchell's (*J. Ind. Eng. Chem.*, 1921, **13**, 806) lead-salt-alcohol method from the mixed fatty acids liberated from the ether-extracted dry soap. The composition of the unsaturated acids was determined from the iodine value and the bromination products, and that of the saturated acids by fractional crystallisation and the examination of the methyl esters of the completely hardened acids.

The hydrogenation of the oil was carried out with nickel-pumice catalyst, and the relation between the refractive index and iodine value of the various samples, taken out at intervals during the process of hydrogenation, was determined.

Tanaka's modified castor-seed-lipase-hydrolysis method showed that while the lipase could effect the hydrolysis of the common oils like sesame, ground-nut, etc., it had no effect on *Bonducella* oil under the conditions of the experiment. This is similar to the action of mustard oil in its inhibiting effect on lipase. This matter is being investigated further.

Experimental.

Constants of Bonducella *Oil (Flem).*

Refractive index	... 1·4750 at 25°.
Saponification value	... 199·5—200·5.
Iodine value (Winkler)	... 127.
Specific gravity	... 0·9215 at 28°/15°C.
Acetyl value	... *Nil.*
Polenske value	... *Nil.*
Hehner number	... 93.
Unsaponifiable matter	... 1·5%

Lewkowitsch (*loc. cit.*) gives the iodine value for oil (*Cæsalpinia Bonducella*, Roxb.) as 89·9, and Bhaduri (*Proc. Chem. Soc.*, 1912, **28**, 53) gives the following figures:—S. V. 292·8, I.V. 96·1, $D_{27}°$ 0·9132.

The fatty acids were liberated by decomposing the ether-extracted dry soap with dilute hydrochloric acid. The fatty acids, free from hydrochloric acid, were heated up to 120° in an atmosphere of carbon dioxide in order to remove the last traces of water.

Constants of the fatty acids.

Mean molecular weight	... 282·5
Iodine value	... 136
Titre value	... 19·2°
Saponification value	... 126·5

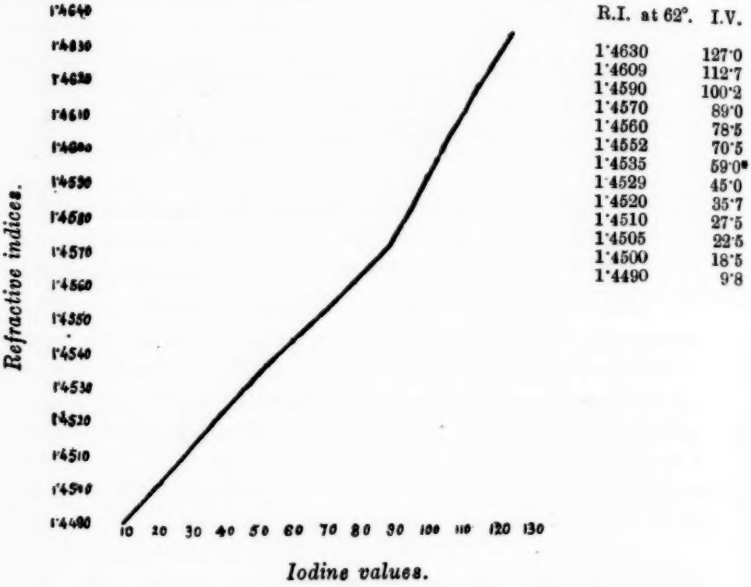
Hydrogenation of the oil.

The hydrogenation was carried out with the nickel-pumice catalyst prepared by reducing the dried nickel carbonate, precipitated on pumice, in a current of hydrogen at 300°. A temperature of 180° was maintained during the hydrogenation and it was noticed in a number of batches that the catalyst did not function at the first attempt. However, when the same sample of the oil treated as above was filtered and charged with fresh catalyst, the hydrogenation proceeded normally. It was also noticed that the stirring was accompanied by much frothing. This does not occur with other common oils like ground-nut, sesame, linseed, etc. These two peculiarities were also particularly noticed in the case of mustard oils when similarly hydrogenated.

Several samples of the oil were removed during the progress of hydrogenation. Their iodine values and refractive indices were determined and the curve showing the relation between them is shown in Fig. I. One point with 59 I.V. falls outside the curve.

FIG. I.

The relation between the refractive indices and iodine values.



The saturated acids.—The saturated acids from the mixed fatty acids were estimated by Twitchell's lead-salt-alcohol method. The percentage of saturated acids was 16 on the total mixed acids with mean molecular weight 269·5 and iodine value practically *nil*. The titre of the saturated acids was 56°.

The unsaturated acids.—The unsaturated acids were obtained by decomposing the lead salts of the liquid acids with dilute hydrochloric acid and extracting them with ether. They formed 84 % of the mixed acids. Their mean molecular weight was 283 and iodine value 157·6.

The unsaturated acids were examined by their bromine additive compounds as recommended by Jamieson and Baughman (*J. Amer. Chem. Soc.*, 1920, **42**, 2398.)

About 5 gm. of the acids were weighed out and dissolved in 100 c.c. dry ether with 2 c.c. glacial acetic acid, cooled in ice and brominated with dry bromine. On cooling the mixture for two hours in ice, no precipitate of hexa-bromide separated out showing the absence of linolinic acid. The ethereal solution was then washed free from bromine with sodium thiosulphate solution, and afterwards freed from the thiosulphate. It was finally dried on anhydrous sodium sulphate, and the total bromides were obtained on evaporation of ether. These were further dried in vacuum and weighed.

In the absence of the hexabromide, which indicates the absence of linolinic acid, the proportion of linoleic to oleic acid works out from the iodine value as 73·92% to 26·08%, which is in agreement with the results obtained from the bromination products shown under the columns A and B in Table I.

TABLE I.

	A	B
Quantity brominated. ...	5·086 gm.	6·250 gm.
Hexabromide.	*Nil.*	*Nil.*
Yield of di- and tetra-bromides. ...	10·201 gm.	12·415 gm.
Calculated yield from above percentage of oleic to linoleic acid. ...	10·150 gm.	12·450 gm.
M.p. of tetrabromide (cryst. from petrol). ...	113°	113°

The composition of the saturated acids.

6·56 Gm. of the saturated acids were subjected to crystallisation from 90% alcohol and separated into two fractions:

(1) 1st crop (*a*) —3·23 gm.; m.p. 57°, M. W. 271.

(2) Recovered from filtrate—3·33 gm.; m.p. 57°, M.W. 263.

According to the mixture tables (*J. Indian Inst. Sci.*, Vol. 6. Part 6, pp. 126—127, Table II; Lewkowitsch "Chemical Technology and Analysis of Oils, Fats and Waxes", 1921, Vol. I, p. 118), (1) and (2) give definite points on the palmitic-stearic mixture curve. The composition of the original saturated acids works out at 63% palmitic and 37% stearic, thus giving in the original oil 10·08% of palmitic and 5·92% of stearic acids.

Crop (*a*) was further crystallised first from acetone and afterwards from a very small quantity of 90% alcohol. Crop (*b*) was thus obtained, having 63° m.p. and 277 M.W. This crop (*b*) also gives a point on the palmitic-stearic curve with 73% stearic and 27% palmitic acids.

Acid (*b*) was further crystallised and after four crystallisations a very small quantity of glistening plates was left when the melting point had risen to 69°. A mixed melting point was taken with pure crystallised stearic acid melting at 69°, M.W. 284 and no lowering of melting point was noticed. This proved that the higher acid present in the mixture was stearic acid.

The composition of the saturated acids was also determined by hydrogenating the original oil, liberating the acids and then examining the methyl esters by fractional distillation under a pressure of 25 mm.

TABLE II.

Refractionation of methyl esters of hardened acids from Bonducella *oil.*

I	II	III	IV	V	VI	VII	VIII	IX
Fraction.	Boiling range.	Weight in gms.	Titre.	Mean M.W.	M.W. of acids calc. from ester value.	M.p. (acids).	Palmitic p.c. from IV, VI & VIII.	Stearic p.c. from IV, VI & VII.
1.	232°	8·6	28·5°	285·1	271·1	60°	40	60
2.	232° 234°	9·97 —	31·5° —	291·2 —	277·2 —	65° —	22 —	78 —
3.	234°	15·05	33·2°	294·5	280·5	66°	15	85
4.	235° 237°	— 29·50	— 34·5°	— 294·6	— 280·6	— 67°	— 10	— 90
5.	237°	35·00	35·2°	298·2	284·2	67°	—	100
Residue.	241° & above	9·12	—	—	—	—	—	92

The values given in columns IV, VI and VII of Table II are in good agreement with the required percentages shown in columns VIII and IX with the exception of fraction 5 where the titre of the ester and the melting point of acids are a degree or so lower than in the case of pure stearic acid. The iodine value of this fraction was found to be 4. This explains its lower melting point. On one crystallisation from alcohol pure stearic acid was obtained. The percentage of the liquid acids from this iodine value being negligible, fraction 5 is treated in the calculation as pure stearic acid. In the

residue the iodine value was found to be 8. The ester was then decomposed, the acids liberated and crystallised from 90% alcohol. In two crystallisations, a clean acid, having m.p. 69° and M. W. 283·6 was obtained showing that the higher acid contained in the residue was stearic acid only. After allowing for the presence of the liquid acids from the iodine value, the whole of the residue was taken to be stearic acid.

From the percentages of the acids the quantities of palmitic and stearic acids were calculated on the weights of the different fractions as given in the following table.

TABLE III.

Fraction.	Wt. of palmitic acid.	Weight of stearic acid.
1	3·44 gm.	5·16 gm.
2	2·19 gm.	7·78 gm.
3	2·25 gm.	12·80 gm.
4	2·95 gm.	26·55 gm.
5	—	35·00 gm.
Residue.	—	8·32 gms.
	10·83 gm.	95·61 gm.

Total = 106·44 gms.

Thus the composition of the hardened acids is 10·16 % palmitic acid and 89·84 % stearic acid. This is in fair agreement with the previous results obtained by direct examination of the saturated acids.

Table IV gives the composition of (*a*) the acids from the hardened oil, (*b*) the mixed acids from the original oil and (*c*) the oil itself.

TABLE IV.

	(*a*) P.c. in hardened acids.	(*b*) P.c. in mixed acids.	(*c*) P.c. of the corresponding glycerides in the oil.
Palmitic acid.	10·16	10·16	10·00
Stearic acid.	89·84	5·84	5·79
Oleic acid.	—	21·91	21·60
Linoleic acid.	—	62·09	61·40
Unsaponifiable matter.	—	—	1·5.

The unsaponifiable matter.

On the extraction of the dry soap with ether in the Soxhlet extractor, a deep yellow coloured residue was obtained which, on being allowed to stand, yielded a yellow needle-shaped crystalline substance with a peculiar odour. This odour was noticed while dealing with the unsaponifiable matter from the Indian soap nut oil. The residue was completely soluble in absolute alcohol and, on crystallisation from 98% alcohol, yielded a crystalline sterol melting at 135°. Viewed under a microscope the crystals showed the characteristic shapes of sitosterol crystals. One of the constituents in the unsaponifiable matter thus appears to be sitosterol.

Summary.

(1) *C. Bonducella* nut kernels yield 20 per cent. of the fixed oil on extraction with petrol ether. The oil has a pale yellow colour and a characteristic odour.

(2) The glucoside separated from the oil-extracted kernel with alcohol contains most of the sulphur of the *Bonducella* nut.

(3) Attempts to separate the alkaloid did not meet with success.

(4) *Bonducella* oil has a poisoning effect on the nickel catalyst similar to mustard oils. The oil is hardened, however, on using a fresh catalyst.

(5) The iodine value—refractive index curve shows a bending near 90 (iodine values). One point with 59 I.V. falls outside the curve.

(6) The acids present are in the form of glycerides of oleic, linoleic, palmitic and stearic acids. The main peculiarity noticed is the large proportion of linoleic to oleic and similarly of palmitic to stearic acid. This is not generally the case with the common oils. Their composition is shown in Table IV.

(7) *Bonducella* oil has an inhibiting action on castor seed lipase.

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Magnetic Susceptibilities of Some Inorganic and Organic Electronic Isomers.

By S. S. Bhatnagar and Sham Lal Luther.

In a recent paper Bhatnagar and Dhawan (*Phil. Mag.*, 1928, **5**, 536) have discussed the following equation :—

$$\chi_m = -2{\cdot}85 \times 10^{10} \times (Kr_1)^2 \quad \ldots \quad \ldots \quad (1)$$

where χ_m is the molecular susceptibility, r_1 the mean radius of the molecule calculated from W. L. Bragg's data in a manner described before (*loc. cit.*) and K is an arbitrary constant. This equation has been shown to hold for a large number of electronic isomers. In order to understand the full significance of the constant K and to bring the above equation into line with the original Langevin equation, Bhatnagar and Mathur put this equation into a modified form in a subsequent publication (*Phil. Mag.*, 1928, **6**, 217). Due to an unfortunate misprint in the first paper the original equation of Langevin in the second paper has been unnecessarily multiplied by $\frac{2}{3}$ and the equation modified by us, when correction is made for this, should read as—

$$\chi_m = -2{\cdot}85 \times 10^{10} \times k\,(r_1)^2 \quad \ldots \quad (2)$$

This equation differs from equation (1) only by the fact that k has been brought out of the brackets from equation (1) and as such k is equal to K^2.

In this paper further experimental evidence has been brought forward in support of equation (2). That value of the constant has been adopted which gives the best possible results with all members in a particular set of electronic isomers. This is justified as the experimental values of susceptibilities are perhaps more or less equally accurate in all cases.

The method employed for the determination of susceptibilities is the one described by Oxley and Wilson and used in our previous papers (*loc. cit.*).

Special precautions were taken to purify the substances chemically as well as magnetically. The accurary of the magnetic balance is within approximately $\pm 10\%$. In Table I are given the values of

susceptibilities and the calculated radii of the molecules from Bragg's data of atomic diameters. The last column shows the susceptibilities as they will come out on calculation by employing the numbers of k and r_1, in equation (2).

TABLE I.

A. Electronic Isomers (Inorganic).

Atomic number.	Names.	Mean values of k calculated from equation (2).	Values of r_1 in A° calc. from Bragg's data.	$-\chi_m \times 10^6$ Experimental.	$-\chi_m \times 10^6$ Calculated from the mean value of k.
46	NaBr	1·3	2·965	30·77	32·56
46	SrO	1·3	2·60	28·02	25·04
78	$AgNO_3$	4·0	1·885	41·19	40·53
78	$CdCO_3$	4·0	1·752	36·02	34·98

B. Electronic Isomers (Organic).

72	Aminobenozic acid* $NH_2.C_6H_6.CO_2H$	10·34	1·717	85·8	86·84
72	Nitrotoluene* $CH_3.C_6H_4.NO_2$	10·34	1·717	87·9	86·84
56	Valeric acid* $C_4H_9.CO_2H$	8·0	1·629	61·09	60·64
56	Propyl acetate* $CH_3.CO.OC_3H_7$	8·0	1·629	60·1	60·64
96	Benzophenone. $(C_6H_5)_2CO$	11·26	1·974	119·9	125·0
96	Galactose. $C_6H_{12}O_6$	11·26	1·834	113·7	107·9
76	Isatin. $C_8H_5O_2N$	9·0	1·735	81·04	77·16
76	Phthalimide. $C_6H_4(CO)_2NH$	9·0	1·735	86·06	77·16
66	Ethylaniline. $C_6N_5NHC_2H_5$	9·74	1·772	87·14	87·18
66	Dimethylaniline. $C_6H_5.N(CH_3)_2$	9·74	1·772	79·34	87·18
66	Collidine. $C_5H_2N(CH_3)_3$	9·74	1·772	83·18	87·18

Before discussing the results it would be interesting to give the values of k for previously described electronic isomers (Bhatnagar and Dhawan ; *Phil. Mag.*, 1928, **5**, 536) and Bhatnagar and Mathur (*Phil. Mag.*, 1928, **6**, 217) as calculated on equation (2) in this paper.

TABLE II.

A. Electronic Isomers (Inorganic).

Atomic number.	Names.	Mean values of k calculated from equation (2).	Values of r_1 in A° calc. from Bragg's data.	$-\chi_m \times 10^6$ Experimental.	$-\chi_m \times 10^6$ calculated from the mean value of k.
28	NaCl*	1	2·825	23·96	22·74
28	CaO*	1	2·35	15·14	15·74
72	CsCl*	1·42	3·425	47·13	47·45
72	KI	1·42	3·475	51·46	48·85
78	TeH_2O_3*	5·5	1·515	33·73	35·97
78	$ZnSO_4$*	5·5	1·646	43·58	42·46

B. Electronic Isomers (Organic).

48	Butyric acid. $CH_3(CH_2)_2CO_2H$	8·69	1·528	60	57·79
48	Ethylacetate. $CH_3CO.OC_2H_5$	8·69	1·528	55	57·79
40	Methylacetate. CH_3COOCH_3	6·59	1·411	35·89	37·89
40	Propionic acid. $CH_3CH_2CO_2H$	6·59	1·411	38 92	37·89
58	Anisole.* $C_6H_5OCH_3$	8·2	1·67	64·98	65·16
58	Benzyl alcohol.* $C_6H_5CH_2OH$	8·2	1·67	65·58	65·16
58	Phenyl hydrazine.* $C_6H_5NHNH_2$	8·2	1·648	62·03	63·45
58	*o*-Cresol.* $CH_3.C_6H_4.OH$	8·2	1·67	65·16	65·16
58	Toluidine. $CH_3.C_6H_4.NH_2$	9·40	1·689	76·37	76·43
58	Methylaniline. $C_6H_5.NHCH_3$	9·40	1·689	76·61	76·43
40	*iso*-Butyl aldehyde $(CH_3)_2CHCHO$	7·54	1·488	47·45	47·6
40	Methyl ethyl ketone. $CH_3COC_2H_5$	7·54	1·488	47·74	47·6
72	Methyl benzoate. $C_6H_5COOCH_3$	9·46	1·754	83·23	82·92
72	Phenyl acetate. $CH_3COOC_6H_5$	9·46	1·754	82·69	89·92
50	Glycerine* $CH_2OH.CHOH.CH_2OH$	8·96	1·502	56·82	57·61
50	Aniline* $C_6H_5.NH_2$	8·96	1·595	65·17	64·97

* For these substances the values of $-\chi_m \times 10^6$ have been taken from the "Physico-chemical Tables" of Landolt and Börnstein. Most of the remaining values have been determined experimentally by Messrs. C L. Dhawan and S. L. Luther. The values of r_1 have been recalculated on the basis of atomic radius of H = 0·53A°.

Discussion of Results.

A close examination of the above table shows three significant relations between the values of k.

(*a*) The values of k tend to increase with the number of atoms contained in the molecule. For example, in the case of molecules having five atoms the value of k is 4. For molecules having 13 atoms it is as great as 7·54 and for those having 24 atoms it is 11·26. In the case of substances marked by (*) the values of k are slightly out of this rule but still the trend is, in general, in the same direction.

(*b*) In the case of groups of isomers having the same number of atoms in the molecule, the values of k increase with the atomic numbers of the groups. For example (NaCl and CaO) and (CsCl and KI) are two groups of electronic isomers having the same number of atoms in the molecule, but having different atomic numbers 28 and 72 respectively. And the value of k in the latter group is greater than that in the former. Similar relations also exist between the groups of electronic isomers having 14, 16, and 17 atoms in the molecule.

(*c*) In the case of groups of electronic isomers having the same atomic number, the values of k increase with the number of atoms as shown in the table below.

TABLE III.

Atomic number.	No. of atoms.	Substance.	Values of k.
	Inorganic isomers.		
78	5	$AgNO_3$	4·0
78	5	$CdCO_3$	4·0
78	6	TeH_2O_3	5·5
78	6	$ZnSO_4$	5·5
	Organic isomers.		
40	11	Methyl acetate.	6·59
40	11	Propionic acid.	6·59
40	13	*iso*Butyl aldehyde.	7·54
40	13	Methyl ethyl ketone.	7·54

Similar relations also exist when the atomic number is 58. A slight discrepancy is observed in the values of k for aminobenzoic acid and nitrotoluene.

The above significant facts about the constant k suggest that equation (2) may be of fundamental physical significance. It is clear from (*a*), (*c*) and (*d*) that the value of k is a function of both the number of atoms in the molecule and its atomic number—an observation that is easily intelligible on the modern concept of diamagnetism.

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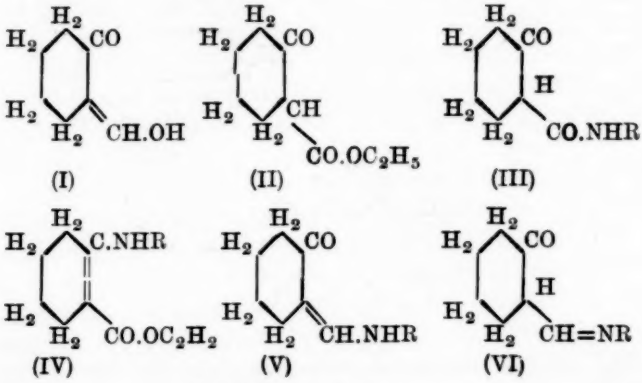
Formation of Heterocyclic Compounds. Part IV. Interaction of Ethyl *cyclo*Hexanone-2-carboxylate with Arylamines. Part I. Synthesis of Tetrahydrophenanthridones.

By Hemendra Kumar Sen and Umaprasanna Basu.

In a previous communication by one of us (Sen and Mondal, *J. Indian Chem. Soc.*, 1928, **5**, 609) it was shown that the generally accepted notion of hydroxymethylene ketones being permanantly enolised β-diketones, cannot be held as being strictly correct. Even their sodium salts have been found capable of reacting with alkyl iodides in both phases (*loc. cit.*). While interesting results are expected from a study of the intensities of absorption in keto-enol equilibria, it was found necessary for the purpose of our work to establish a reasonable chemical difference between β-diketones and hydroxymethylene ketones in condensation reactions, although the inherent defect of the chemical method of handling equilibrium mixtures cannot but be recognised.

In the present investigation the behaviour of ethyl *cyclo*hexanone-2-carboxylate (II) with aniline and substituted anilines has been studied. It is obvious that there are two centres of reaction with aniline both in (I) and (II), namely at the acid part as also at the ketonic group. In the case of (II), the reaction of aniline at the ester part would invariably give rise to an anilide (III), whilst in the case of (I), both anilide (V) and anil (VI) may be formed:—



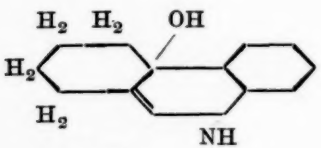
R=An aryl group.

A comparison of the absorption spctra of the compound obtained by the interaction of aniline and hydroxymethylene *cyclo*hexanone with those of the aniline and anil of *cyclo*hexanone carboxylate, showed that the hydroxymethylene derivative is distinctly analogous to the anil (IV). Further study in this direction is in progress.

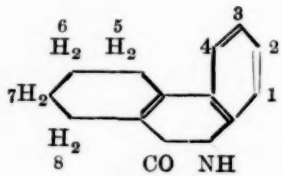
Whilst the anilides (III) of the keto-ester gave a violet coloration with alcoholic ferric chloride, neither the anil (IV) of the ester nor the aniline derivative of the hydroxymethylene *cyclo*hexanone gave any coloration. This behaviour can be explained from their respective structural formulæ. It would be noticed that neither in (IV) nor in (V) there is any labile hydrogen atom to enolise a keto group which is at the bottom of ferric chloride reaction. This is further corroborated by the fact that the amount of absorption is far more in (III) than in (IV) and (V) as should be expected from the enolic structure of (III). Besides, the *ortho*-quinonoid structure of (V) would require it to be coloured. As a matter of fact, it is a bright yellow compound whereas (IV) is almost colorless.

The direct consequence of the absence of enolising hydrogen in (V) may account for its inability to form ring compounds under the influence of sulphuric acid. Repeated attempts to prepare (VII) failed in our hands (*cf.* Borsche, *Annalen*, 1910, **377**, 70).*

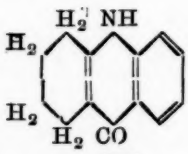
On the other hand, the anilide (III) of ethyl *cyclo*hexanone-2-carboxylate, on being heated with concentrated sulphuric acid for a short time, gives a good yield of the 5 : 6 : 7 : 8-tetrahydrophenanthridone derivative (VIII).



(VII)



(VIII)



(IX)

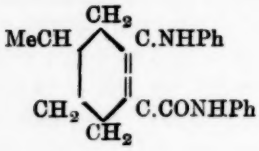
*Thielepape (*Ber.*, 1922, **55**, 131), however, records two cases where inspite of the presence of enolising hydrogen, ring closure could not be effected. In the light of the present work, his experiments need repetition.

As the tetrahydrophenanthridones form a new class of compounds, they were synthesised from various anilides of ethyl *cyclo*hexanone-2-carboxylate. As a β-ketonic ester, ethyl *cyclo*hexanone 2-carboxylate may react in two ways giving rise to either (III) or (IV) (*cf.* Conrad and Limpach, *Ber.*, 1887, **20**, 944 ; 1891, **24**, 2990 ; Knorr, *Ber.*, 1883, **16**, 2593 ; 1884, **17**, 540 ; 1887, **20**, 1397 ; *Annalen*, 1886, **236**, 69 ; 1888, **245**, 378 ; Knorr and Reuter, *Ber.*, 1894, **27**, 1169 ; Besthorn and Garben, *Ber.*, 1900, **33**, 3439 ; Dieckmann, *Annalen*, 1901, **317**, 91 ; Ewins and King, *J. Chem. Soc.*, 1913, **103**, 104 ; Thielepape, *Ber.*, 1922, **55**, 131. In order to obtain pure products on the one hand, and products of known constitution on the other, the first step in this syntheses was to know the constitution of the products of the reaction with the amines definitely. An anil (IV) would give rise to a tetrahydroacridone derivative (IX) whereas an anilide (III) would yield tetrahydrophenanthridone (VIII).

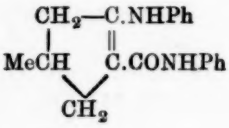
On heating ethyl *cyclo*hexanone-2-carboxylate (1 mol.) with a primary arylamine (1 mol.) at 190-200° for periods varying from 2 to 30 minutes at first a solid product is isolated which on purification gives a violet coloration with an alcoholic solution of ferric chloride indicating thereby the presence of an enolic group and as such pointing to the anilide (and not anil) constitution of the product. The other reason which has lead us to the conclusion that this reaction product is an anilide, is that the compound when dissolved in concentrated sulphuric acid and heated for 20 minutes on a water-bath, is transformed into a tetrahydrophenanthridone derivative. The corresponding isomeric compound tetrahydro-acridone is known and described by Tiedtke (*Ber.*, 1909, **42**, 631) as colorless needles, m.p. 258°. Our compound obtained from ethyl *cyclo*hexanone-2-carboxylate-anilide crystallises in fine prismatic needles melting at 273°. It would be important now to distil it with zinc dust to obtain phenanthridine itself. This will be undertaken as soon as the quantity of material permits.

It may be mentioned here that many years ago Kötz and Merkel (*J. pr. Chem.*, 1909, (*ii*), **79**, 102) succeeded in transforming ethyl 5-methyl-*cyclo*hexanone-2 carboxylate into its anilino-anilide derivative (X) by boiling it with aniline. These authors also heated ethyl *cyclo*hexanone-2-carboxylate with aniline and obtained a compound which they described as ethyl 2-anilido-$\triangle^1$-*cyclo*hexene-1-carboxylate (IV, R=Ph) melting at 29°. Reference may be made in this connection to a compound described by Dieckmann (*loc. cit.*) which he

obtained by heating ethyl 4-methyl-*cyclo*pentanone-2-carboxylate with aniline (2 mols.) and described it as an anilino-anilide (XI).

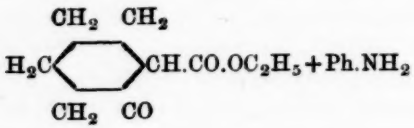


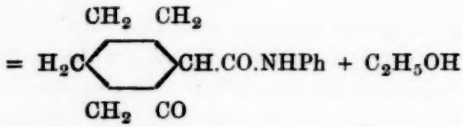
(X)

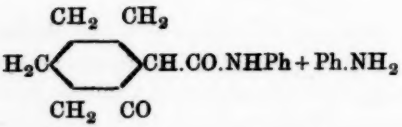


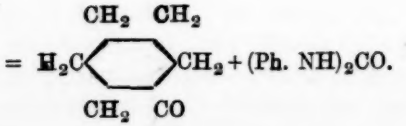
(XI)

But by working under the conditions described in the experimental portion of this paper, no such compound was isolated whether the ester was allowed to react with 2 mols. of aniline or with one molecule. If instead of equimolecular proportions of the keto-ester and a primary amine, 2 molecules of the latter and one molecule of the former are heated above 150° for several hours, the product separating from the liquid is a diaryl carbamide derivative whilst the mother-liquor retains the anilide similar and identical in properties to the anilides obtained in other ways. The yield of the carbamide derivative varies between 30 and 50 per cent. of the weight of the amine used (*cf.* Oppenheim and Precht, *Ber.*, 1876, **9**, 1098). The reaction in our case may be expressed as below:—









In our experiments, the simultaneous formation of the carbamide derivative and the anilide would point to the conversion of the latter into the former, a view also held by Knorr (*Annalen*, 1886, **236**, 69) who isolated diaryl carbamides by distilling the anilides.

All the tetrahydro-phenanthridones, described in this paper, are crystalline solids of high melting points. They are insoluble in alkali but dissolve in concentrated sulphuric acid giving colorless solutions without fluorescence, from which they are again precipitated on dilution with water.

Whilst generally high temperatures give rise to anilides, the interaction of the keto-ester and the aryl amines at ordinary temperature yields the corresponding anils.* Thus *p*-amino-acetanilide when reacted with the keto-ester in acetic acid solution yields a well crystalline product which imparts no coloration to alcoholic ferric chloride. This fact and the analytical result prove it to be an anil. Similarly by reacting the keto-ester with aniline, a product has been isolated which melts at 57·5° and does not give any coloration with alcoholic solution of ferric chloride. This is also provisionally accepted as an anil. Further work to prove its constitution by converting it into known tetrahydro-acridone (IX) (*loc. cit.*) is in progress.

Experimental.

Ethyl cyclo*Hexanone-2-carboxylate and Anilline.*

(i) *Formation of* cyclo*Hexanone-2-carboxylate-anilide*. (*Formula* III, R = Ph).—Ethyl *cyclo*hexanone-2-carboxylate (4 g.) and aniline (2·2 g.) were heated under reflux at 185° for about half an hour in an oil-bath. The mass after reaction was washed with dilute hydrochloric acid and taken up in ether. The ethereal solution, on drying and evaporating, left a viscous liquid which, after several washings with petroleum ether, yielded a granular solid. The substance was crystallised by dissolving in ether and diluting the solution with petroleum ether in which solvent the compound was insoluble. (Found: N, 6·72. $C_{13}H_{15}O_2N$ requires N, 6·45 per cent.).

It melts at 104-105° and is soluble in most organic solvents and to some extent in warm water, but it is insoluble even in strong

* The reaction between aniline and methyl benzoylacetate at 150°, however, for a long time gives rise to a mixture of β-phenylamidophenylacrylic anilide (NHPh. CPh :CH.CO.NHPh) and benzoylacetic anilide (Ph.CO.CH_2.CONHPh). (Knorr, *Annalen*, 1888, **245**, 378).

caustic soda solution. In alcoholic solution it gives with ferric chloride a fine violet coloration. The anilide when heated with concentrated sulphuric acid for a few minutes on a water-bath, yields tetrahydrophenanthridone (described below) on pouring the acid solution into water.

(*ii*) *Formation of Diphenylcarbamide.*—A mixture of ethyl *cyclo*hexanone-2-carboxylate (2 g.) and aniline (2·2 g.) was heated under reflux on an oil-bath for 7 to 8 hours at 150-160°. Next day fine needles (1·1 g.) were collected. These crystallised from rectified spirit in flaky needles, m. p. 235°. (Found: N, 13·32. $C_{13}H_{12}ON_2$ requires N, 13·21 per cent.).

The identity of the compound was established by taking a mixed melting point with diphenylcarbamide.

(*iii*) *Formation of* 5:6:7:8-*Tetrahydrophenanthridone* (VIII).—The ester and aniline were heated in molecular proportion at 190° for an hour. The liquid was then repeatedly washed with dilute hydrochloric acid and then with petroleum ether for several times. A viscous liquid was left behind. Without isolating the substance, it was treated with concentrated sulphuric acid for 20 minutes at the temperature of the boiling water-bath. The red solution was poured into water when a white solid was obtained. It crystallises from glacial acetic acid, diluted with a few drops of water, in fine prismatic needles melting at 273°. (Found: N, 7·07. $C_{13}H_{13}ON$ requires N, 7·03 per cent.).

The substance is insoluble in alkali but dissolves in concentrated sulphuric acid forming a colorless solution without fluorescence, from which it is precipitated unchanged on dilution with water. Its isomeric compound tetrahydroacridone (IX) was also prepared by heating *cyclo*hexanone with anthranilic acid according to the method of Tiedtke (*loc. cit.*). A mixture of this and our compound melted at 255°.

Ethyl cyclo*Hexanone-2-carboxylate and* p-*Toluidine.*

(*i*) *Formation of Di-p-tolylcarbamide.*—The ester (2 g.) and *p*-toluidine (2·5 g.) were heated together for 7 hours at 160°, the carbamide derivative separating after 3 hours' heating (yield, 1 gm.). It crystallises from rectified spirit in flakes melting at 260°. (Found: N, 11·88. $C_{15}H_{16}ON_2$ requires N, 11·66 per cent.).

(*ii*) *Formation of* cyclo*Hexanone-2-carboxylate-p-toluidide.* (*Formula* III, R = *p*-Tol).—The di-*p*-tolylcarbamide obtained by heating a mixture of the ester (2 g.) and *p*-toluidine (2·5 g.) at 160° for 3

hours was filtered off. The mother-liquor was then washed with dilute hydrochloric acid, and on scratching the residual liquid, a solid was obtained. This was filtered and washed with petroleum ether and dried. Its ethereal solution being once treated with animal charcoal was allowed to evaporate. The crystals thus obtained were washed with petroleum ether when they melted at 108-109°. (Found: N, 6·46. $C_{14}H_{17}O_2N$, requires N, 6·06 per cent.).

The substance is insoluble in alkali; in an alcoholic solution, it gives with ferric chloride a violet coloration.

(*iii*) *Formation of* 3-*Methyl*-5:6:7:8-*tetrahydrophenanthridone*.—A molecular proportion of the ester (2 g.) was mixed with the molecular proportion of *p*-toluidine (1·25 g.) and the mixture was heated for 2 minutes at 192-193° on an oil-bath. The red liquid obtained was washed with dilute hydrochloric acid when, on scratching, a solid was isolated. It was filtered, dried and washed with petroleum ether. The substance thus obtained (1·1 g.) on crystallisation melted at 108°. The mixed m.p. of this with that previously obtained was also 108°. It gave the usual color reaction with ferric chloride and was insoluble in alkali.

The toluidide thus obtained was dissolved in concentrated sulphuric acid (3 c.c.) and the solution was heated on a boiling water-bath for 20 minutes, and then poured into water (40 c.c.) when a white crystalline solid separated out. The yield was quantitative. The substance crystallises from glacial acetic acid diluted with water in fine prismatic needles, melting at 286-288°. (Found: N, 6·68. $C_{14}H_{15}ON$ requires N, 6·57 per cent.).

The compound gives no color reaction with ferric chloride and is insoluble in alkali but dissolves in concentrated sulphuric acid forming a colorless solution without flourescence.

Ethyl cyclo*Hexanone*-2-*carboxylate and* m-*Xylidine* (*asymmetric*).

(*i*) *Formation of Di*-m-*xylylcarbamide*.—A mixture of the ester (2 g.) and xylidine (2·8 g.) was heated for 4½ hours at 180° when about 1 g. of the condensation product was obtained. The carbamide began to separate after 1½ hours' heating. Crystallising from alcohol it melted at 262°. (Found: N, 10·65, $C_{17}H_{20}ON_2$ requires N, 10·45 per cent.).

(*ii*) *Formation of* cyclo*Hexanone*-2-*carboxylate*-m-*xylidide*.—A mixture of the ester (4 g.) and xylidine (5·7 g.) was heated under reflux for 4½ hours at 170-180°. The solid separated was filtered

off. The filtrate was washed with dilute acid when on scratching the residual liquid a solid was isolated. It was collected and washed with petroleum ether. Yield 2 gms. It was crystallised from methyl alcohol with the addition of animal charcoal. Recrystallised from the same solvent with a few drops of water, it melted at 125-126°. (Found: N, 5·88. $C_{15}H_{19}O_2N$ requires N, 5·71 per cent.).

This xylidide is a well crystallised substance, insoluble in alkali and alkaline carbonate; on boiling the solution, however, the substance goes readily into solution in the former but with difficulty in the latter. In alcoholic solution it gives with ferric chloride a violet coloration.

(*iii*) *Formation of* 1:3-*Dimethyl*-5:6:7:8-*tetrahydrophenanthridone*.—A mixture of ester (2 g.) and the xylidine (1·42 g.) was rapidly heated up to 200° for 2 minutes. On cooling a solid mass was obtained. It was washed with dilute hydrochloric acid and then with petroleum ether (yield, 1 g.). It melted at 123°. The mixed m.p. of it with the anilide previously obtained is 124-125°.

The anilide (1 g.) on usual treatment with sulphuric acid gave 0·9 gm. of the phenanthridone, m.p. 270-71° (from glacial acetic acid). (Found: N, 6·29. $C_{15}H_{17}ON$ requires N, 6·17 per cent.).

The substance is soluble in concentrated sulphuric acid without any coloration and flourescence.

Ethyl cyclo*Hexanone*-2-*carboxylate and* β-*Naphthylamine*.

(*i*) *Formation of Di-*β*-naphthylcarbamide*.—The ester (2 g.) was heated with β-naphthylamine (3·3 g.) at 170° for three hours. The crystals separated were filtered off and washed with ether. Yield 0·8 gm. The expected β-dinaphthylcarbamide was crystallised from amyl acetate when it melted at 301-302°.

(*ii*) *Formation of* cyclo*Hexanone*-2-*carboxylate*-β-*naphthylamide*.—The filtrate from the above reaction was treated with dilute hydrochloric acid and the solid (2·5 g.) separated was collected. It was washed with petroleum ether and crystallised from alcohol using animal charcoal. Recrystallised from the same solvent, it melted at 149°. (Found: N, 5·38. $C_{17}H_{17}O_2N$ requires N, 5·24 per cent.).

It is insoluble in sodium carbonate solution, and in alcoholic solution it gives with ferric chloride the usual violet coloration.

(*iii*) *Formation of* 3:4-*Benzo*-5: 6: 7: 8-*tetrahydrophenanthridone*.—A mixture of the ester (2 g.) and β-naphthylamine (1·7 g.)

was heated at 205° for 2 minutes. The viscous mass obtained was repeatedly washed with hot benzine when about 1·1 g. of the substance (m.p. 145°) were obtained. The mixed m.p. with that previously obtained was 148-149°. It also gave the usual chemical reactions.

From 1 gm. of this substance 3: 4-benzo-5: 6: 7:8-tetrahydrophenanthridone was obtained by the usual method (yield, 0·7 gm.). It crystallises from glacial acetic acid diluted with a few drops of water; m.p. 291°-292°. (Found: N, 5·70. $C_{17}H_{15}ON$ requires N, 5·62 per cent.).

Ethyl cyclo*Hexanone-2-carboxylate and α-Naphthylamine.*

(*i*) *Formation of Di-α-naphthylcarbamide.*—The ester (2 g.) and the amine (3·4 g.) were heated together at 170-180° for 3 hours, the solid separating even after half an hour. The mass was cooled and repeatedly washed with boiling alcohol to remove any unchanged α-naphthylamine. The residue was crystallised from amyl acetate in which di-α-naphthylcarbamide was somewhat soluble. It melted at 288°. (Found: N, 9·17. $C_{21}H_{16}ON_2$ requires N, 8·97 per cent.).

Ethyl cyclo*Hexanone-2-carboxylate and* p-*Aminoacetanilide.*

(*i*) *Formation of* cyclo*Hexanone-2-carboxylate-*p-*acetaminoanilide.* (*Formula* III, R= C_6H_4NHAc (para).—A mixture of the keto-ester (4 g.) and *p*-aminoacetanilide (3·6 g.) was heated at 185-190° for about half an hour when a thick sludge was obtained. On rubbing the mass with dilute hydrochloric acid, a solid (about 3·6 gm.) was isolated. It crystallises from dilute alcohol in fine crystals melting at 182·5°. (Found: N, 10·04. $C_{15}H_{18}O_3N_2$ requires N, 10·2 per cent.).

The substance is soluble in boiling caustic soda solution and gives with ferric chloride in alcoholic solution the characteristic violet coloration of the anilides. Here it should be noticed that the first product separating from the reaction mixture is the anilide itself and the yield is about 55-60 per cent. of the theory.

(*ii*) *Formation of Ethyl* 2-p-*Acetaminoanilido-*$\triangle^1$-cyclo*hexene-*1-*carboxylate.* (*Formula* IV, R= C_6H_4.NHAc (para).—Molecular proportions of the keto-ester and *p*-aminoacetanilide were taken in glacial acetic acid solution and the flask being corked was left overnight. Next day a beautiful crystalline compound was found. This was collected and the mother-liquor, on concentration and afterwards dilution with water, gave another crop of the same

substance (total yield, about 40 per cent.). The substance crystallises from alcohol in small glistening flakes. As the substance and the solution were found to be colored, the latter was twice treated with animal charcoal, but the final product still retained a light yellow tinge. (Found: N, 9·5. $C_{17}H_{23}O_3N_2$ requires N, 9·27 per cent.).

This compound melts at 191·5°, and imparts no coloration to alcoholic ferric chloride. A mixture of this with the anilide (m.p. 182·5°) melted at 159°.

Ethyl cyclo*Hexanone-2-carboxylate and Aniline.*

(i) *Formation of Ethyl 2-Anilido-*$\triangle^1$*-cyclohexene-1-carboxylate* (IV, R=Ph).—The keto-ester (8 g.) and the aniline (4·4 g.) were mixed together and left overnight. Next day the mixture was found to be turbid owing to the separation of water. The flask was left for 3 days in a vacuum over fused calcium chloride. Fine crystalline solid began to separate. After a week the contents set to a hard mass which was collected and dried over porous plate (10·5 gm.). It crystallises from methyl alcohol in prisms with a very light yellow tinge and melts at 57·5° (sharp). The mixed m.p. with the corresponding anilide previously obtained was 54°. It gives no coloration with alcoholic ferric chloride. It dissolves in ether, alcohol and even in petroleum ether in which the corresponding anilide is insoluble.

The compound is provisionally regarded as a compound similar to that described by Kötz and Merkel (*loc. cit.*) who, however, recorded a melting point of 29°.

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Received March 6, 1929.

REVIEWS

The Chemistry of Water and Sewage Treatment by ARTHUR M. BUSWELL, Chief, Illinois State Water Survey, Professor of Sanitary Chemistry, University of Illinois (1928). (The American Catalog Co. Inc. New York).

This book is one of the American Chemical Society series of Scientific and Technologic monographs. It presents in an admirable way the chemical reactions underlying water treatment processes, and supplies such diagrams as would help the reader to follow large scale operations without much previous experience. The first chapter —Notes on Chemical Theory—and the second on Colloids give a very clear exposition of the physico-chemical points that have to be attended to in modern water treatment investigations. The Chapters on sewage treatment and disposal, the chemical and biochemical aspects of the activated sludge process and sludge digestion are all very ably written, with a very useful number of bibliographic references. It is a book which a water and sewage works engineer, a chemist as also a biochemist will read with profit.

H. K. S.

Chemistry of Leather Manufacture, Second edition, Vol. I by JOHN ARTHUR WILSON. (The American Catalog Co. Inc. New York).

The book is a record of the recent researches on leather chemistry done by the author and other leather chemists. The subject has been presented in an exceedingly interesting and readable from so as to make it intelligible even to chemists who have not specialised in the applied chemistry of leather manufacture. To the leather chemists the book is invaluable in as much as it gives them information on most of the important problems in connection with tanning chemistry.

The many experiments quoted in the book are not only highly instructive but will act as an incentive to investigators and stimulate thought and further research.

The chapters on the Histology of skins and Physical Chemistry of Proteins have been very lucidly written and will be found very instructive. The Photo-micrographs are invaluable to both leather chemists and practical tanners.

The importance of *p*H value in the various operations connected with tanning has been illustrated by figures and curves which will not fail to carry conviction.

Details of analytical methods and tanning processes have been mostly omitted. This is a deviation from the line that has hitherto been followed by authors of books on tanning. Their inclusion would have made the book unwieldy and would not have increased its usefulness to research workers in the field of leather chemistry.

In brief the book has been well conceived, well written and has filled up a real gap in the modern tanning literature.

B. M. D.

=20

Coagulation of Gelatin Sols in Alcohol-Water Mixture.

By S. Ghosh, S. N. Banerjee and N. R. Dhar.

It is well-known that isoelectric gelatin can be coagulated by alcohol. Fenn (*J. Biol. Chem.*, 1918, **33**, 270) found that the presence of acids, alkalis and salts hinders the precipitation of gelatin by alcohol. It is interesting to note from the results of Loeb ("Proteins and the Theory of Colloidal Behaviour," 1922, p. 252) that with acidified gelatin, which behaves like a positively charged colloid, far greater amounts of electrolytes with polyvalent cations (*e.g.* $CaCl_2$, $BaCl_2$, $AlCl_3$ etc.) are required than NaCl, KCl, etc., inspite of the fact that for positively charged sols only chloride ions are potent in coagulating the sols. Polyvalent cations possess an inhibiting action on the precipitation of acidified gelatin in alcohol-water mixture. Similarly, with alkaline gelatin, which behaves like a negatively charged sol, polyvalent anions from electrolytes like Na_2SO_4, $Na_2C_2O_4$, $Na_4Fe(CN)_6$, etc., also possess an inhibiting action on its precipitation. These results of Loeb seem to indicate that the valency of the ions carrying a charge similar to that on the colloid particles is an important factor in the coagulation of gelatin in alcohol-water mixture.

In previous publications (*J. Phys. Chem.*, 1925, **29**, 435, 659; 1927, **31**, 187; *Kolloid Z.*, 1924, **34** 262; 1925, **36**, 131) we have shown that the sols which are capable of adsorbing appreciable amounts of the similarly charged ion from the precipitating electrolyte require larger quantities of the electrolyte for precipitation. We have also proved that these sols show abnormal dilution effect, *viz.* greater amounts of an electrolyte are necessary for coagulation of diluted sols than concentrated ones, develop 'ionic antagonism' when coagulated by mixtures of electrolytes and show the phenomenon of positive acclimatization.

In order to throw light on the nature of gelatin we have investigated (*a*) the influence of dilution of the gelatin sol in alcohol-water on its coagulation, and (*b*) precipitation with mixtures of electrolytes, and (*c*) the phenomenon of acclimatization.

Positively charged gelatin sol in alcohol-water mixture.—Purified gelatin (Goldruck, Kahlbaum) containing 0·1% ash and p_H value 5·3 was used. Five gm. of gelatin were dissolved at 80° in 50 c.c. of water, and 12·5 c.c. *N*/8-HCl were added and the total volume was made up to 500 c.c. with absolute alcohol. The p_H value of aqueous gelatin of the same concentration in presence of 12·5 c.c. *N*/8 -HCl was also determined and found to be 4·4.

The opalescent gelatin sol in alcohol-water mixture was sensitive to electrolytes and it was found that water has a remarkable stabilising influence. 4 C.c. of the gelatin sol and 0·5 c.c. of the coagulating electrolytes were separately taken and then mixed up and left for half an hour when the coagulation was observed.

Influence of dilution on the coagulation of positively charged gelatin sol in alcohol-water mixture.

The sol is diluted with 87·5% alcohol which is the amount present in the original sol (Sol A).

TABLE I.

Electrolyte.	Amount to coagulate in c.c.		
	Sol A.	Sol A/2.	Sol A/3.
KCl *N*/10	0·26	0·43	>0·50
K_2SO_4 *N*/50	0·25	0·22	0·18
$K_4Fe(CN)_6$ *N*/100	0 42	0·36	0·30
HCl *N*/25	0·35	>0·50	—
$MgCl_2$ *N*/2·5	0·26	0·48	—

The above table shows that the sol becomes stable on dilution when coagulated by KCl, HCl and $MgCl_2$. The sol could not be coagulated by $Al(NO_3)_3$ and the opalescence disappears when the electrolyte is added to the sol. Barium chloride also behaves like $Al(NO_3)_3$ and the sol could be coagulated only by a saturated solution of $BaCl_2$. Smaller concentrations of HCl and $MgCl_2$ also make the sol clear.

TABLE II.

Coagulation with a mixture of KCl *and* K_2SO_4.

Amount of $N/10$ -KCl added in c.c.	Amount of $N/50$-K_2SO_4 required for coagulation in c.c. Observed.	Calculated.	Difference.
0·26	0	—	—
0	0·25	—	—
0·05	0·24	0·20	+0·04
0·10	0·21	0·16	+0·05
0·15	0·17	0·11	+0·06

TABLE III.

Coagulation with a mixture of $MgCl_2$ *and* K_2SO_4.

Amount of $N/20$-$MgCl_2$ to coagulate in c.c.	Amount of $N/50$-K_2SO_4 required for coagulation in c.c. Observed.	Calculated.	Difference.
0·26	0	—	—
0	0·25	—	—
0·05	0·26	0·20	+0·06
0·10	0·24	0·16	+0·08
0·15	0·22	0·11	+0.11

TABLE IV.

Coagulation with a mixture of $BaCl_2$ *and* KCl.

$BaCl_2$, $N/20$ added in c.c.	...	0	0·05	0·10
Amount of $N/10$-KCl required for coagulation in c.c.	...	0·26	0·30	0·38

TABLE V.

Coagulation with a mixture of HCl *and* KCl.

$N/2·5$-HCl added in c.c.	Amount of $N/10$-KCl to coagulate in c.c. Observed.	Calculated.	Difference.
0	0·26	—	—
0·35	0	—	—
0·05	0·28	0·22	+0·06
0·10	0·27	0·19	+0·08

TABLE VI.

Coagulation with a mixture of HCl *and* K_2SO_4.

$N/2·5$-HCl added in c.c.	Amount of $N/50$-K_2SO_4 required to coagulate in c.c. Observed.	Calculated.	Difference.
0	0·25	—	—
0·35	0	—	—
0·05	0·28	0·21	+0·07
0·10	0·28	0·18	+0·10

TABLE VII.

Coagulation with a mixture of $Al(NO_3)_3$ *and* KCl.

$N/20$-$Al(NO_3)_3$ added in c.c. ...	0	0·05	0·10
Amount of KCl to coagulate in c.c. ...	0·26 of $N/10$	0·33 of $N/10$.	0·22 of $N/5$.

The results recorded in Tables II, III, V and VI show that the phenomenon of 'ionic antagonism' appears when gelatin in alcohol-water mixture is coagulated with $KCl+K_2SO_4$, $MgCl_2+K_2SO_4$, $HCl+K_2SO_4$, and $HCl+KCl$. The sol is remarkably stabilised in presence of $BaCl_2$ and $Al(NO_3)_3$ when coagulated by KCl.

In order to investigate the phenomenon of acclimatization by an electrolyte, 4 c.c. of the sol were treated with 0·04 c.c. of the electrolyte at a time after every fifteen minutes till coagulation was observed. The coagulation was investigated one hour after the last addition of electrolyte. The amount necessary to coagulate the sol, when the electrolyte was added all at once, is determined by pouring the whole of the required electrolyte to 4 c.c. of the sol and the coagulation was observed after one hour. The following results were obtained.

TABLE VIII.

Electrolyte.	Amount required to coagulate when added slowly in c.c. (0·4 c.c. at a time).	Amount to coagulate when added all at once in c.c.
KCl $N/20$	0·36	0·30
HCl $N/2·5$	0·28	0·20
$MgCl_2$ $N/5$	0·38	0·30
K_2SO_4 $N/100$	0·28	0·30

The results in the foregoing table show that appreciable amount of positive acclimatization is developed when the sol is coagulated by KCl, HCl and $MgCl_2$. Very slight negative acclimatization is developed with K_2SO_4.

Negatively charged gelatin sol in alcohol-water mixture.—0·5 Gm. of gelatin was dissolved in 5 c.c. of water at 80° and 2·5 c.c. of *N*/10-KOH. The solution is made up to 500 c.c. with absolute alcohol. The p_H value of 0·1 % gelatin solution in presence of 2·5 c.c. of *N*/10-KOH is found to be 7·90. The gelatin sol in alcohol-water mixture is opalescent. The following results were obtained on the coagulation of the sols of different concentrations.

Influence of dilution on the coagulation of negatively charged sol in alcohol-water mixture.

TABLE IX.

The sol is diluted with the same percentage of alcohol-water mixture as present in the original sol.

Electrolyte.	Amount to coagulate in c.c.		
	Sol A.	Sol A/2.	Sol A/3.
KCl *N*/10	0·32	0·28	0·26
K_2SO_4 *N*/5	0·30	0·32	0·35
$K_4Fe(CN)_6$ *N*/5	0·24	0·25	0·25
$BaCl_2$ *N*/100	0·30	0·18	0·15
$MgCl_2$ *N*/50	0·25	0·18	0·15
KOH *N*/3·5	0·22	0·30	0·36
HCl *N*/50	0·26	0·20	0·15
$Al(NO_3)_3$ *N*/100	0·25	0·20	0·15

The above results show that the sol behaves abnormally towards dilution when coagulated by K_2SO_4, $K_4Fe(CN)_6$ and KOH; on the other hand, it behaves normally towards dilution when coagulated by KCl, $BaCl_2$, $MgCl_2$ and HCl. When amounts of $Al(NO_3)_3$ or HCl slightly greater than the precipitating concentrations are added to the sol, it becomes clear and charge reversal is observed. Amounts of KOH smaller than the precipitating concentration also make the sol clear.

TABLE X.

Coagulation with a mixture of KCl *and* $BaCl_2$.

Amount of *N*/10-KCl added in c.c.	Amount of $BaCl_2$ to coagulate in c.c.		
	Observed.	Calculated.	Difference.
0	0·30	—	—
0·32	0	—	—
0·05	0·24	0·25	−0·01
0·10	0·18	0·20	−0·02

There is no ' ionic antagonism ' when the sol is coagulated with mixtures of KCl and $BaCl_2$.

TABLE XI.

Coagulation with mixtures of K_2SO_4 *and* $MgCl_2$.

Amount of *N*/5-K_2SO_4 added in c.c.	Amount of *N*/50-$MgCl_2$ to coagulate in c.c.		
	Observed.	Calculated.	Difference.
0	0·25	—	—
0·30	0	—	—
0·05	0·21	0·21	0
0·10	0·18	0·17	+0·01
0·15	0·15	0·13	+0·02

Very slight ' ionic antagonism ' is observed when the sol is coagulated with a mixture of K_2SO_4 and $MgCl_2$.

TABLE XII.

Coagulation with mixtures of KOH *and* KCl.

Amount of *N*/15-KOH added in c.c. ...	0	0·05	0·10
Amount of N/10-KCl to coagulate in c.c. ...	0·32	0·35	0·40

The foregoing results show that the sol is appreciably stabilised towards its coagulation by KCl in presence of KOH.

Experiments on the phenomenon of acclimatization were made with the negatively charged sol as was done with the positively charged sol. The following results were obtained.

TABLE XIII.

Electrolyte.	Amount to coagulate when added slowly in c.c. (0·04 c c. at a time).	Amount to coagulate when added all at once in c.c.
KCl *N*/10	0·24	0·25
K_2SO_4 *N*/10	0·28	0·25
$BaCl_2$ *N*/200	0·32	0·40
$MgCl_2$ *N*/100	0·28	0·35
KOH *N*/3 5	0·24	0·15
HCl *N*/100	0·16	0·20
$Al(NO_3)_3$ *N*/200	0·20	0·30

From the above table it will be seen that the phenomenon of positive acclimatization is slightly developed when the sol is coagulated by K_2SO_4 whilst considerable amount of negative acclimatization is developed when the sol is coagulated by $BaCl_2$, $MgCl_2$, HCl and $Al(NO_3)_3$. The phenomenon of positive acclimatization is, however, developed with KOH.

Discussion.

Our experimental results with a positively charged sol of gelatin show that it could not be coagulated by $BaCl_2$ and $Al(NO_3)_3$ and these electrolytes also exert remarkable antagonistic action towards the coagulation of the sol by KCl. The amounts of HCl and $MgCl_2$ required to coagulate the sol are greater than that of KCl and small concentrations of these electrolytes stabilise the sol, and antagonistic action is developed when the sol is coagulated by mixtures of $K_2SO_4+MgCl_2$, HCl+KCl, and HCl+K_2SO_4. Slight 'ionic antagonism' is also observed when the sol is coagulated with mixtures of KCl and K_2SO_4. The sol becomes stable on dilution when coagulated by KCl, $MgCl_2$ and HCl. It is also observed that KCl, $MgCl_2$ and HCl develope the phenomenon of positive acclimatization with the positively charged sol of gelatin in alcohol-water mixture.

In previous publications we have shown that if an ion carrying the same charge as the colloid particle is absorbed by the sol from an electrolyte the following should result:—

(*i*) Adsorption of the similarly charged ions would increase the charge on the colloid particles and consequently inhibit the action of the oppositely charged ion, which causes coagulation.

(*ii*) The ratio of the amounts of adsorption of the similarly charged ions to that of oppositely charged ions increases with the dilution of the sol, and this results in the stability of the sol on dilution towards its coagulation by the electrolyte.

(*iii*) The percentage of adsorption of similarly charged ions is greater from a dilute solution than from a concentrated one. This causes ' ionic antagonism ' and the phenomenon of positive acclimatization.

It appears, therefore, from Tables I-VIII that a sol of acidified gelatin in alcohol-water mixture can adsorb K°, $Ba^{\circ\circ}$, $Mg^{\circ\circ}$, H° and $Al^{\circ\circ\circ}$ ions.

From the results of Loeb on the coagulation of negatively charged sol of gelatin in alcohol-water mixture, it will be found that the amounts of K_2SO_4, K_3-citrate, $K_4Fe(CN)_6$, etc., necessary for coagulation are greater than that of KCl. This points to the conclusion that anions, SO_4'', $Fe(CN)_6''''$ and $Citrate'''$ are adsorbed in greater amounts than Cl', when the amount adsorbed is expressed in equivalent. Our results on the coagulation of the negatively charged sol with mixtures of KCl and $BaCl_2$ show that no ionic antagonism is developed, and the sol behaves normally towards dilution when coagulated by these electrolytes separately. On the other hand, slight ' ionic antagonism ' is developed when the sol is coagulated with mixtures of K_2SO_4 and $MgCl_2$, showing that SO_4'' ions possess an inhibiting action on the coagulation of the sol. The sol also becomes stable on dilution when coagulated by K_2SO_4. Considerable amount of ' ionic antagonism ' is developed when the sol is coagulated with mixtures of KOH and KCl. The sol behaves abnormally on dilution when coagulated by KOH. The phenomenon of acclimatization studied with the negatively charged sol of gelatin in alcohol-water mixture show that whilst positive acclimatization is observed with K_2SO_4 and KOH, slight negative acclimatization is observed with KCl and it is more pronounced with $BaCl_2$, $MgCl_2$, HCl and $Al(NO_3)_3$. In papers published from these laboratories (*J. Phys. Chem.*, 1925, **29**, 659; 1927, **31**, 649; *Kolloid Z.*, 1926, **37**, 141; *J. Indian Chem. Soc.*, 1928, **5**, 313) we have shown that when a sol can adsorb the oppositely charged ions in large amounts, so that the adsorption of the similarly charged ions is comparatively small, the phenomenon of negative acclimatization is developed. We are, therefore, of opinion that a negatively charged sol of gelatin can adsorb appreciable

amounts of anions like SO_4'', citrate,''' OH', $Fe(CN)_6'''$ from K_2SO_4, K_3-citrate, KOH and $K_4Fe(CN)_6$, but the amount of adsorption of anions from KCl, $MgCl_2$, $Al(NO_3)_3$, $BaCl_2$ and HCl is not at all significant in comparison with the amount of adsorption of cations from these electrolytes.

Gelatin, being an amino acid, can behave both as an acid and a base, and therefore, can adsorb both cations and anions. We have, however, shown in this paper that gelatin prefers to take up a cation more easily than an anion. Thus we have shown in this paper that gelatin sol in alcohol-water mixture can adsorb appreciable amounts of cations like $Ba^{\circ\circ}$, $Al^{\circ\circ\circ}$, $Mg^{\circ\circ}$, etc., whether it is charged positively or negatively, because the acidic character of gelatin is more pronounced than the basic and it exerts an affinity for the adsorption of cations. We have also observed that polyvalent cations are required in very large amounts to coagulate a positively charged sol of gelatin and can very easily bring charge reversal of the negatively charged sols, whilst polyvalent anions cannot bring about charge reversal of the positively charged sol. This is because gelatin can take up more cations than anions. It is well known that the p_H value of the isoelectric gelatin is 4·70 and that gelatin begins to behave as a base, when the medium is distinctly acidic. This also indicates that gelatin possesses greater acidic properties than basic, and is therefore capable of adsorbing comparatively larger amounts of cations than anions.

From Fenn's results it will be seen that polyvalent cations possess a stabilising influence for the positively charged sol and the polyvalent anions have a stabilising effect on the negatively charged sol of gelatin in alcohol-water mixture. Loeb has shown that isoelectric gelatin is more easily dissolved in an electrolyte containing either a polyvalent cation or a polyvalent anion. We are of opinion that these observations of Fenn and Loeb originate from the property of gelatin which can adsorb both polyvalent cations and anions.

Perrin (*J. Chim. phys.*, 1904, **2**, 601; 1905, **3**, 50) has observed that salts with trivalent cations can reverse the charge of negatively charged membranes and that tetravalent anions cause the reversal of charge of positively charged membranes. Leob (*J. Gen. Physiol.*, 1921-22, **4**, 463) has found that $LaCl_3$ and $CeCl_3$ or $K_4Fe(CN)_6$ makes a film of isoelectric gelatin to assume an electric charge either positive or negative due to the adsorption of $La^{\circ\circ\circ}$ and $Ce^{\circ\circ\circ}$ ions or $Fe(CN)_6''''$ ion.

Our experimental results on the coagulation of gelatin sol in presence of either alkali or acid in alcohol-water mixture show that the negatively charged sol can adsorb anions like SO_4'', $Fe(CN)_6''''$, OH', etc., and the positively charged sol can adsorb cations like $Ba^{\circ\circ}$, $Al^{\circ\circ\circ}$, H°, etc. Loeb, however, believes that only cations can be taken up by gelatin containing alkali and that only anions can be adsorbed by gelatin containing acid. On the other hand, Pauli (*Fortschr. naturwiss. Forschung*, 1912, **4**, 223) holds that both ions of a salt are adsorbed by a protein.

Loeb considers that the effect of ions like $Ca^{\circ\circ}$, $La^{\circ\circ\circ}$, etc., in inhibiting the precipitation of positively charged gelation sol in alcohol-water arises from the increasing effect of these ions on the forces of attraction between water and gelatin. It is generally believed that great hydration is associated with marked stability of the sol. In previous papers (*Kolloid Z.*, 1928, **44**, 149; *J. Indian Chem. Soc.*, 1928, **5**, 303) we have shown that hydration of sols need not be a significant factor for the stability of sols. Leob ("Proteins and the Theory of Colloidal Behaviour," 1922, p. 91) has shown that the viscosity of gelatin sol is markedly decreased in presence of neutral salts and this shows that the degree of hydration of the sol is decreased by the addition of electrolytes. In several communications (*J. Phys. Chem.*, 1925, **29**, 1556; 1926, **30**, 1646; *Kolloid Z.*, 1928, **44**, 225); from this laboratory we have shown that sols become less viscous on the addition of small quantities of electrolytes due to the increase of their electric charge by the adsorption of similarly charged ions. Hence the decrease of the viscosity of gelatin by the addition of neutral salts appears to be due to the adsorption of similarly charged ions.

Summary and Conclusion.

(1) Positively charged gelatin sol in alcohol-water mixture behaves abnormally towards dilution when coagulated by KCl, HCl and $MgCl_2$ and it could not be coagulated by $BaCl_2$ and $Al(NO_3)_3$.

(2) The sol develops 'ionic antagonism' when coagulated by mixtures of KCl and K_2SO_4, $MgCl_2$ and K_2SO_4, HCl and K_2SO_4, and HCl and KCl, and is markedly stabilised in presence of $BaCl_2$ and $Al(NO_3)_3$ when coagulated by KCl.

(3) The above sol shows positive acclimatization when coagulated by KCl, HCl and $MgCl_2$.

(4) Negatively charged gelatin sol in alcohol-water mixture behaves abnormally towards dilution when coagulated by K_2SO_4, $K_4Fe(CN)_6$ and KOH and behaves normally towards dilution when coagulated by KCl.

(5) Negatively charged sol shows, no 'ionic antagonism' when coagulated by mixtures of KCl and K_2SO_4, and 'ionic antagonism' is observed slightly when coagulated by mixtures of K_2SO_4 and $MgCl_2$. KOH stabilises the sol when it is coagulated by KCl.

(6) The phenomenon of positive acclimatization is observed with negatively charged sol when coagulated by K_2SO_4 and KOH, whilst marked negative acclimatization is developed when the sol is coagulated by HCl, $BaCl_2$, $MgCl_2$ and $Al(NO_3)_3$.

(7) Our results show that positively charged gelatin can adsorb cations and negatively charged gelatin, the anions, but gelatin adsorbs more of a cation than an anion. Similarly charged ions, therefore, play an important role in the coagulation of positively and negatively charged gelatin in alcohol-water mixture.

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Further Action of Magnesium Amalgam on Nitrates and its Action on Nitrous acid, and Salts of the Oxyacids of Sulphur and the Halogens.

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The action of magnesium amalgam on nitrates has been studied by Neogi and Nandi (*J. Chem. Soc.*, 1928, **133**, 1449) who have shown that, besides hydroxylamine and ammonia, hyponitrites of the respective metals are formed. Several new hyponitrites have been isolated by this method. The success of this method for the preparation of hyponitrites lies in the fact that magnesium hydroxide, which is formed as a product of the reaction, being insoluble in water, is easily removed, and unlike caustic soda formed in Divers' sodium amalgam method, does not decompose the hyponitrites obtained as a result of the reduction of nitrates and nitrites. In this paper this method of preparing hyponitrites has been extended to other metals such as thallium, beryllium, uranium, aluminium, cerium and thorium, with the hope of being able to isolate their hyponitrites. From the experimental results given below, it would be observed that uranium, beryllium and cerium yielded unstable hyponitrites, which could not be isolated in the pure condition, as their solution readily underwent decomposition during concentration. Thallium, aluminium, and thorium do not form any hyponitrites, their hydroxides being obtained in the insoluble precipitate. Hydroxylamine was obtained in solution in the case of cerium only whilst ammonia was obtained in all cases.

The action of magnesium amalgam on nitrous acid gave a very unusual though interesting result. Free nitrous acid solution was prepared by the action of ice water on liquid N_2O_3. On treating this below 5° with magnesium amalgam, no hydroxylamine and very little ammonia were produced but magnesium nitrite was formed in the pure state, any nitrate accompanying the nitrite undergoing reduction to the latter.

The action of magnesium amalgam on the salts of the oxyacids of sulphur and the halogens was next studied. It was found that

sulphates were not reduced by magnesium amalgam. Though sulphites are reduced by zinc and hydrochloric acid, neither sulphites nor bisulphites were reduced by magnesium amalgam even at 50° even when the reduction was carried on for several hours. Thiosulphates, however, were easily reduced to a mixture of sulphite and sulphide with the evolution of hydrogen sulphide. Dithionates remained practically unaffected, whilst persulphates yielded a mixture of sulphates, the mercury being simultaneously oxidised in the process to yellow mercuric oxide.

To investigate the action of magnesium amalgam on the salts of the oxyacids of the halogens its action on chlorates, bromates, iodates, perchlorates and periodates was studied. Chlorates and perchlorates remain unaffected even at 50°. Bromates were completely reduced to bromides and iodates to iodides, no intermediate reduction product such as hypobromite being obtained even when the reduction was effected in ice-cold solutions. Potassium periodate was reduced first to iodate and then to iodide.

Experimental.

Beryllium hyponitrite.—Magnesium amalgam was prepared according to the method of Neogi and Nandi (*loc. cit.*). The five per cent. amalgam was cut into small pieces and stored in stoppered bottles and used when necessary.

Five gm. of beryllium oxide were dissolved in hot dilute nitric acid keeping a slight excess undissolved. The resultant solution of beryllium nitrate was cooled in ice and salt and the magnesium amalgam added in small quantities. The temperature was not allowed to rise above 5°. The precipitate was filtered off in a filter pump and the solution again treated with magnesium amalgam. This was repeated three or four times and the reduction was continued until the solution was free from nitrate and nitrite. The solution did not contain any hydroxylamine or hyponitrite. The precipitate was washed with cold water and treated with dilute acetic acid (1 : 15) until the greater part of the precipitate dissolved. The solution responded to the tests of both beryllium and hyponitrite, showing that beryllium hyponitrite was insoluble in water. Attempts were next made to obtain the compound in the pure state but without success. Part of the solution was neutralised with ammonia in the cold but no precipitate of beryllium hyponitrite was obtained.

The acid as well as the neutral solutions were then kept in a vacuum desiccator over sulphuric acid in an ice chest surrounded with ice and salt. Both the solutions gave tests for hyponitrites for one or two days but during further concentration the hyponitrite decomposed. Repeated attempts to obtain the pure hyponitrite proved equally unsuccessful owing to the decomposition of the hyponitrite when concentrated even in ice chests.

Uranium hyponitrite.—Uranyl nitrate (5—6 gm.) was dissolved in water in a beaker immersed in ice and salt. The cold solution was treated with small quantities of magnesium amalgam in the same way as in the case of beryllium. The temperature was maintained below 5° throughout. When the reduction was continued for some time, the whole of the uranium was precipitated. The solution contained hydroxylamine and also magnesium nitrite. The precipitate was washed with water and dissolved in cold dilute acetic acid (1 : 15) and was found to contain hyponitrite. The solution thus obtained , even when concentrated in an ice chest in a vacuum desiccator over sulphuric acid, did not yield any hyponitrite of uranium. Duriug concentration, the solution responded to the tests for hyponitrites for one or two days; and a yellow precipitate gradually formed which, when washed and dissolved in dilute acetic acid in the cold, did not give any test for hyponitrite. The yellow precipitate was found to be uranyl hydroxide. Repeated attempts to isolate the hyponitrite in a pure condition resulted in failure, owing to the decomposition of the hyponitrite during concentration. The uranium in the hyponitrite is possibly present in the uranyl condition, for the acetic acid solution of the hyponitrite gave with ammonia or caustic alkalis the yellow precipitate of ammonium or alkali diuranate. It is very curious, however, that uranyl compounds which are so readily reduced to the uranous condition even with sulphuretted hydrogen, should remain in the uranyl condition in the presence of nascent hydrogen. Had it been an uranous compound aikalis would have precipitated uranous hydroxide which turns black on heating.

An interesting observation is that when the acetic acid solution of the hyponitrite was kept at the ordinary temperature for some hours in air so as to allow all the hyponitrite to decompose, part of the resulting solution when treated with silver nitrate yielded a reddish brown precipitate which was undoubtedly not a hyponitrite. This precipitate was washed and on examination

was found to contain only uranium and silver, and no acid. The precipitate was found on analysis to be silver diuranate. The ratio of uranium to silver actually found is 2·22 : 1, the calculated ratio being 2·21 : 1.

The same acetic acid solution after the decomposition of the hyponitrite when treated with lead nitrate solution yielded a yellow precipitate containing only lead and uranium and no acid. The precipitate on analysis was found to be lead diuranate. The ratio of uranium to lead actually found is 2·31 : 1, the calculated value being 2·29 : 1.

Cerium hyponitrite.—A concentrated solution of cerium nitrtae cooled in freezing mixture was reduced with magnesium amalgam in the usual way. After reduction for about three hours the solution became free from cerium and was found to contain hydroxylamine. The precipitate was washed with cold water and taken up with cold dilute acetic acid (1 : 15). The acetic acid solution was found to contain both cerium and hyponitrite, thereby showing that the cerium hyponitrite is insoluble in water. On carefully neutralising the acetic acid solution with cold dilute ammonia no precipitate of cerium hyponitrite was obtained. When preserved in a vacuum desicator over sulphuric acid in an ice chest, the hyponitrite decomposed in a day showing the instability of cerium hyponitrite.

Reduction of the nitrates of thallium, aluminium and thorium.

In these cases no hyponitrite was formed either in the solution or in the precipitate and no hydroxylamine was obtained. The results in each case are briefly tabulated below.

Aluminium nitrate.—A solution of aluminium nitrate was treated with magnesium amalgam in the usual way. In a short time the whole of the aluminium was precipitated as hydroxide and the solution was found to contain magnesium nitrate but no hydroxylamine or hyponitrite. The precipitate on solution in dilute cold acetic acid also did not yield any hyponitrite.

Thallium nitrate.—A solution of the thallium nitrate on reduction with magnesium amalgam in the usual way yielded thallous hydroxide in solution which contained no hydroxylamine or hyponitrite. The precipitate on solution in dilute acetic acid in the cold did not give any test for hyponitrites.

Thorium nitrate.—The results in the case of thorium nitrate were analogous to those of aluminium nitrate. In a short time the

solution on reduction with magnesium amalgam became free from thorium and contained no hydroxylamine. The solution of the precipitate in dilute acetic acid gave no test for a hyponitrite.

Action of magnesium amalgam on nitrous acid.—Preparation of pure magnesium nitrite.

Hampe (*Annalen*, 1863, **125**, 295) and Lang (*J. pr. Chem.*, 1863, **86**, 299) prepared magnesium nitrite from equivalent quantities of barium nitrite and magnesium sulphate. Vogel (*Z. anorg. Chem.*, **35**, 385) studied the constitution of crystallised magnesium nitrite and his method of preparation was the same as that of his predecessors but differed only a little in details as regards the method of crystallisation. Rây (*J. Chem. Soc.*, 1905, **87**, 178) studied the action of heat on magnesium nitrite but he also adopted the same method of preparation.

The action of magnesium amalgam on free nitrous acid gave an unusual result. This can be used as a method for the preparation of pure magnesium nitrite. Nitrogen trioxide prepared by the action of nitric acid on arsenious oxide was passed through an empty wash-bottle immersed in cold water to arrest nitric acid and then through a condensing tube immersed in a freezing mixture of ice and salt where it condensed to a blue liquid. This was brought into solution with ice cold water introduced slowly into the condensing tube by means of a pipette. The solution of nitrous acid containing a little nitric acid was placed in a beaker immersed in ice and salt and was carefully treated with magnesium amalgam keeping the temperature below 5°. After some time the solution became neutral and was found to contain magnesium nitrite (and a little nitrate) but no hydroxylamine or hyponitrite. The reduction was continued until the solution ceased to give tests for a nitrate with diphenylamine. A portion of this solution after dilution with ice cold water gave on analysis by Crum's nitrometer method the following result.

1 C.c. of the solution gave 14·3 c.c. of nitrogen gas from the solution at N.T.P.

1 ,, ,, ,, ,, 14·4 ,, NO ,, ,, ,,

thus showing that it was a solution of pure magnesium nitrite containing no nitrate. When the reduction was carried still further, however, hydroxylamine was formed in the solution and magnesium hyponitrite was detected in the precipitate.

This process may be adopted as a standard method for preparing pure magnesium nitrite, which, has hitherto been prepared by pre-

vious investigators by the double decomposition of barium nitrite and magnesium sulphate. In the present method it is necessary to use magnesium amalgam and not pure magnesium as the latter acts very slowly on the solution of nitrous acid and invariably yields a mixture of magnesium nitrite and nitrate. It is magnesium amalgam which reduces any nitrate formed and ensures the formation of pure nitrite.

It will be useful here to summarise the work previously done by Neogi and Nandi (*loc. cit.*) and also the results recorded in this paper on the preparation of hyponitrites, by the action of magnesium amalgam on metallic nitrates and nitrites. As has already been pointed out, this method has the advantage of the absence of caustic soda which decomposes metallic hyponitrites and therefore made it possible to isolate new hyponitrites. The following is a tabular statement of the metals of the various groups of the periodic classification, the hyponitrites of which have been isolated by this method.

TABLE I.

I	II	III	IV	V	VI
Li	Be*				
Na	Mg*				
K	Ca				
	Zr				
Rb	Sr				
	Cd				
Cs	Ba	Ce*			
			Pb		
					U*

Action of magnesium amalgam on chlorates, bromates, iodates, perchlorates and periodates.

Sodium and potassium chlorates.—The solution of the chlorate was acted upon by magnesium amalgam in the cold. There is no advantage in using ice water and the temperature was generally kept between 50° and 60°. It is remarkable that neither sodium nor potassium chlorate, which is reduced to chloride by heating with

The hyponitrites of these metals were not obtained in the pure condition.

zinc and dilute sulphuric acid, sulphurous acid, ferrous sulphate, zinc dust and Devarda's alloy, is reduced by such a powerful reducing agent as magnesium amalgam.

Potassium perchlorate.—A solution of the perchlorate was treated with magnesium amalgam, at 50°-60°. The resulting solution did not contain either chlorate or chloride. This is not to to be wondered at as perchlorates are not reduced by the reducing agents mentioned above.

Sodium bromate.—A solution of sodium bromate was treated with magnesium amalgam in a similar manner, and was quantitatively reduced to sodium bromide.

Sodium iodate and potassium periodate.—A solution of sodium iodate was reduced by magnesium amalgam in the usual way and was found to be reduced to iodide quantitatively, the operation taking about two hours, the temperature being kept about 50°. This reaction is similar to the reduction of an iodate by zinc dust or Devarda's alloy.

A solution of potassium periodate was similarly reduced with magnesium amalgam. At first the periodate was reduced to ar iodate, the latter then undergoing reduction to iodide, no iodine being liberated at any stage of the reaction.

Action of magnesium amalgam on salts of the oxyacids of sulphur.

Sodium and potassium sulphates.—A solution of either sulphate when treated with magnesium amalgam even for a whole day did not yield any sulphite or sulphide in the solution.

Sodium sulphite and bisulphite.—It was expected that sulphites in solution would be reduced to sulphide by magnesium amalgam, but a solution of sodium sulphite when acted on by magnesium amalgam for many hours at 50°-60° failed to produce any sodium sulphide. Sodium bisulphite behaved in a similar manner.

Sodium dithionate.—Otto has shown that sodium dithionate is reduced to sodium sulphite by sodium amalgam and it was expected that magnesium amalgam would produce a similar reaction, but a solution of sodium dithionate when acted upon by magnesium amalgam at 50°-60 for 6-7 hours failed to produce any sulphite or sulphide.

Sodium thiosulphate.—A solution of sodium thiosulphate was treated with magnesium amalgam in the usual manner. The result-

ing solution contained both sulphide and sulphite whilst sulphuretted hydrogen was also evolved, being formed by hydrolysis of the sodium sulphide. This reaction is similar to that reported by Spring with sodium amalgam and thiosulphates.

Potassium persulphate.—When a solution of potassium persulphate was treated with magnesium amalgam in the usual way a vigorous reaction took place. The resultant solution contained a mixture of magnesium sulphate and potassium sulphate and a precipitate of yellow oxide of mercury was formed.

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Photochemical Reaction between Cinnamic Acid and Chlorine in Carbon Tetrachloride Solution.

By Kali Pada Basu.

There is a great deal of controversy at present regarding the primary action of light on chlorine. One school (Chapman, *Trans. Faraday Soc.*, 1925, **21**, 547) holds that activated chlorine molecules are primarily formed. Franck (*Trans. Faraday Soc.*, 1925, **21**, 536), suggests that absorption of light of shorter wavelength than 4785A°, the long wavelength limit of the continuous absorption region, leads to the dissociation of a chlorine molecule into an excited and a normal atom. Weigert (*Z. physikal. Chem.*, 1923, **106**, 407), on the other hand, postulates that the presence of moisture in chlorine is essential for the primary photochemical process and that in its absence the light absorbed by chlorine molecules is given out as isochromatic fluorescence.

The present investigation was taken up with a view to throw some light, if possible, on the action of light on chlorine, and forms the first communication on a series of photochemical reactions involving chlorine undertaken by the present author.

Nasareff (*Z. wiss. Phot.*, 1919, **18**, 231), determined the temperature coefficient of the action of chlorine on cinnamic acid in white light and found it to be 1·4. The bromination has been done in this laboratory by Ghosh and Purakayastha (*J. Indian Chem. Soc.*, 1927, **4**, 409).

Chlorine, in these experiments, was prepared by the action of pure hydrochloric acid on potassium permanganate, washed successively through water, sulphuric acid, anhydrous carbon tetrachloride in an all-glass apparatus and then dissolved in pure dry carbon tetrachloride. The carbon tetrachloride was guaranteed to be free from sulphur and was freed from traces of moisture by shaking with and keeping over anhydrous calcium chloride and redistillation. This is a very important step as will appear presently.

Before chlorination experiments can be profitably followed in carbon tetrachloride solutions, one must be sure that there is no reaction between chlorine and carbon tetrachloride as is claimed

by Plotnikow (*Z. wiss. Phot.*, 1919, **19**, 22). It was found that solutions of chlorine in ordinary carbon tetrachloride showed a slow reaction whereas perfectly dry carbon tetrachloride was not affected by chlorine either in darkness or in light. This is in agreement with the observations of Benrath and Hertel (*Z. wiss. Phot.*, 1924, **23**, 30). Presence of traces of moisture in Nasareff's carbon tetrachloride probably accounts for the slow reaction between cinnamic acid and chlorine in the dark.

Experimental.

Merck's "extra pure" cinnamic acid was further purified by crystallising twice. The reaction vessel employed was a cell (1 cm. in length and breadth and 1 cm. depth) made of optically pure glass. It had a very narrow opening at the top provided with a closely fitting stopper. The velocity of the reaction was determined by pipetting out 2 c.c. from time to time and followed iodometrically with N/500 sodium thiosulphate which was freshly prepared and standardised before each experiment. Preliminary experiments at 22·6° with $M/60$ chlorine solutions in the reaction cell indicated that loss due to evaporaton as 2 c.c. were successively withdrawn by a pipette was negligible.

The Dark Reaction.

At 22·6°, the temperature at which most of the experiments in light were carried out, the dark reaction, as Table I will indicate, was negligible.

Table I.

The Dark Reaction.

Cinnamic acid = $M/30$;	Chlorine = $M/80$;			Temp. = 22·6°.
Time in mins. ...	0	115	330	1260
$N/500$ Thiosuphate in c.c. ...	25·0	21·9	24·4	22·4
Unimol. const. log $a/(a-x)$...			·00004	·00004

The photochemical investigations were carried out with a quartz mercury lamp as the source of light. The chlorination was very slow with a 1000 c. p. Point-o-lite lamp as the source. The kinetics of the reaction was studied in white light with a 4 cm.

water filter, the reaction cell being at a distance of 12 cm. from the mercury lamp which was run from a storage battery with a constant current of 3 amp. The reaction cell was maintained at a constant temperature by placing it inside a double-jacketted copper box through which water at a constant temperature from a thermostat was circulated by means of a pump. As the following tables will show the light reaction is perfectly unimolecular with respect to chlorine, and the value of the constant is independent of the concentration of chlorine. A large number of experiments were carried out, only a few typical results are appended. The unimolecular constants are all on the basis of logarithms to the base 10 and the time is reckoned in minutes.

TABLE II.

Cinnamic acid = $M/30$; Chlorine = $M/60$; Temp. = 22·6°.

Time in mins. ...	0	15	35	55	80	
$N/500$ Thiosulphate in c.c.	34·1	29·8	24·8	20·6	17·0	
Unimol. const. ...		·0039	·0040	·0040	·0038	Mean ·0039

TABLE III.

Cinnamic acid = $M/30$; Chlorine = $M/100$; Temp. = 22·6°.

Time in mins. ...	0	15	35	60	85	
$N/500$ Thiosulphate in c.c.	21·2	18·35	15·5	12·55	10·0	
Unimol. const. ...		·0042	·0039	·0038	·0038	Mean ·0039

TABLE IV.

Cinnamic acid = $M/30$; Chlorine = $M/175$; Temp. = 22·6°.

Time in mins. ...	0	10	25	45	75	
$N/500$ Thiosulphate in c.c.	11·4	10·45	9·2	7·95	5·95	
Unimol. const. ...		·0038	·0037	·0035	·0038	Mean ·0037

Experiments showed that the reaction was zero-molecular with respect to cinnamic acid. The value of the unimolecular constant

was unaffected when the concentration of cinnamic acid was the same as or even lower than the concentration of chlorine. Tables V, VI and VII will make it clear.

TABLE V.

Cinnamic acid = $M/60$; Chlorine = $M/60$; Temp. = 22·6°.

Time in mins. ...	0	15	35	60	85	
$N/500$ Thiosulphate in c.c.	34·2	30·0	24·9	19·25	15·4	
Unimol. const. ...		·0038	·0039	·0041	·0040	Mean ·00395

TABLE VI.

Cinnamic acid = $M/100$; Chlorine = $M/110$; Temp. = 22·6°.

Time in mins. ...	0	15	35	62	85	
$N/500$ Thiosulphate in c.c.	18·75	16·45	13·9	11·2	9·5	
Unimol. const. ...		·0038	·0037	·0036	·0035	Mean ·0036

TABLE VII.

Cinnamic acid = $M/100$; Chlorine = $M/60$; Temp. = 22·6°.

Time in mins.	$N/500$ Thiosulphate in c.c.		Unimol. constant.
0	34·35	...	...
10	31·8	·0034	...
25	27·85	·0036	·0038
45	23·30	·0037	·0039
65	19·30	·0038	·0039
	Mean	·0036	·0039

If, however, the concentration of cinnamic acid employed was very low ($M/150$), the value of the unimolecular constant diminished. Table VIII will make it clear.

TABLE VIII.

Cinnamic acid = $M/150$; Chlorine = $M/100$; Temp. = 22·6°.

Time in mins. ...	0	15	35	55	79	
$N/500$ Thiosulphate in c.c.	19·9	18·1	16·1	14·45	12·2	
Unimol. const. ...		·0027	·0026	·0025	·0027	Mean ·0026

Experiments were then performed in monochromatic light to determine the temperature coefficient and the quantum efficiency of the reaction and to see how these varied with the wavelength of incident light. The following filters, recommended by Weigert ("Optische Methoden der Chemie," 1928, p. 62) were employed.

For 436 $\mu\mu$.—(1) Rhodamin B (0·0075 gm.) and 2 gm. quinine sulphate and 6 c. c. N-H_2SO_4 in 100 c.c.—2 cm. layer.

(2) Water filter—2 cm.

For 404 $\mu\mu$.—(1) Diamant fuchsine (big crystals. 0·03 gm.) and 4 gm. quinine hydrochloride in 100 c.c. of 96 % alcohol,—2 cm. layer.

(2) Copper sulphate (30 gm. in 100 c.c.)—2 cm. layer.

For 366·5 $\mu\mu$.—By giving a preliminary exposure to a photographic plate in a quartz spectrograph it was found that the glass cells employed transmitted the lines 366·5$\mu\mu$ almost undiminished. Transmission began to diminish after 350$\mu\mu$ and ceased altogether at 324$\mu\mu$. The following filters were employed.

(1) Nitrosodimethylaniline (0·0007 %) and methyl violet R—2 cm.

(2) Copper sulphate (50 gm. in 100 c. c.)—2 cm.

The light transmitted at 404$\mu\mu$ and at 366·5$\mu\mu$ was very feeble. The intensity measurements were carried out with a Moll-thermopile and a Moll-galvanometer calibrated with a Hefner lamp at a distance of 100 cm. Although several experiments were carried out only one experiment at each wavelength is appended since the velocity constant is independent of the concentration of the acid and chlorine.

TABLE IX.

Experiment at 436$\mu\mu$.

Intensity of the incident light—2·3 Hefners at 100 cm.

Cinnamic acid = $M/60$; Chlorine = $M/83$; Temp. = 22·6°.

Time in mins. ...	0	53	145	267	363	
$N/500$ Thiosulphate in c.c.	24·6	23·4	21·7	19·5	18·0	
Unimol. const. ...		·00041	·00038	·00038	·00037	Mean ·00038

Since the dark reaction had a constant (*vide* Table I) equal to 0·00004, the pure light reaction constant equals 0·00034.

TABLE X.

Experiment at 404μμ.

Intensity of the incident light—0·25 Hefners at 100 cm.

Cinnamic acid = $M/60$; Chlorine = $M/87$; Temp. = 22·6°.

Time in mins. ...	0	60	210	347	
$N/500$ Thiosulphate in c.c.	22·9	22·2	20·8	19·5	
Unimol. const. ...		·00022	·00020	·00020	Mean ·00021

The pure light reaction constant is, therefore, 0·00017.

TABLE XI.

Experiment at 366·5μμ.

Intensity of the incident light—0·2 Hefners at 100 cm.

Cinnamic acid = $M/60$; Chlorine = $M/83$; Temp. = 22·6°.

Time in mins. ...	0	60	150	270	380	
$N/500$ Thiosulphate in c.c.	24·05	23·2	22·05	20·8	19·5	
Unimol. const. ...		·00026	·00025	·00024	·00024	Mean ·00025

The light reaction constant, therefore, amounts to 0·00021.

Quantum efficiency at different wave-length.—Light absorbed by chlorine was found out by taking a galvanometer reading with the reaction cell filled with carbon tetrachloride and the latter filled with the chlorine solutions of the requisite strength. The difference gave the light absorbed. The Hefner lamp at 100 cm. corresponding to an energy of 900 ergs. per sq. cm. per sec. (Gerlach's value) gave a galvanometer deflection of 100 mm. A deflection of 1 mm. therefore, corresponded to 9 ergs. per sq. cm. per sec.

Wave-length 436 μμ.—The light absorbed corresponded to 24 mm. of galvanometer deflection. No. of quanta absorbed per sq. cm. per sec. therefore,

$$= 24 \times 9 \times \frac{436 \times 10^{-7}}{3 \times 10^{10}} \times \frac{1}{6{\cdot}5 \times 10^{-27}} = 4{\cdot}8 \times 10^{13}$$

The change in chlorine concentration (Table IX) equals 1·2 c.c. $N/500$ in 2 c.c. in 53 mins. Of this 34/38 represents the light reaction. No. of mols. changed per sq. cm. per second

$$= \frac{1\cdot2}{2} \times \frac{34}{38} \times \frac{1}{53\times60} \times \frac{1}{1000\times1000} \times 6\cdot1\times10^{23}$$

$$= 1\cdot01\times10^{14}.$$

The quantum efficiency is, therefore, equal to 2 mols. per quantum.

Wave-length 404 $\mu\mu$.—The light absorbed corresponded to 6 mm. No. of quanta absorbed per sq. cm. per second

$$= 6\times9\times\frac{404\times10^{-7}}{3\times10^{10}}\times\frac{1}{6\cdot5\times10^{-27}} = 1\cdot1\times10^{13}.$$

The change in chlorine concentration (Table X) equals 0·7 c.c. $N/500$ in 2 c.c. in 60 mins. Of this 17/21 represents light reaction. Number of molecules transformed per sq. cm. per second, therefore, amounts to $4\cdot7\times10^{13}$. The quantum efficiency is, therefore, 4 molecules per quantum.

Wave-length 366·5 $\mu\mu$.—The light absorbed amounted to 5 mm. No. of quanta absorbed per sq. cm. per second, therefore, equals $8\cdot4\times10^{12}$. The number of molecules transformed per sq. cm. per sec. (Table XI) amounts to $6\cdot0\times10^{13}$. The quantum efficiency is thus 7 mols. per quantum.

The quantum efficiency is thus very near to unity at 436$\mu\mu$., and gradually increases with the increase in frequency.

Temperature coefficient at different wave-lengths.

Before we can be certain about the light reaction at 32·6° we must determine the dark reaction and the loss of chlorine by evaporation at that temperature. Table XII indicates the dark reaction at 32·6°.

TABLE XII.

Dark Reaction.

Cinnamic acid = $M/60$; Chlorine = $M/83$; Temp. = 32·6°.

Time in mins. ...	0	30	114	205	372
$N/500$ Thiosulphate in c.c.	23·9	23·8	23·6	23·1	22·7
Unimol. const. ...		·00006	·00005	·00007	·00006 Mean ·00006

Experiments were then carried out in monochromatic lights of the same intensity as before. Only one result at each wave-length is given.

TABLE XIII.

Experiment at 436μμ.

Cinnamic acid = $M/60$; Chlorine = $M/83$; Temp. = 32·6°.

Time in mins. ...	0	55	145	250	330	
$N/500$ Thiosulphate in c.c.	23·85	22·3	19·9	17·7	15·8	
Unimol. const. ...		·00053	·00054	·00052	·00054	Mean ·00053

The light reaction constant is, therefore, 0·00047.

TABLE XIV.

Experiment at 404μμ.

Cinnamic acid = $M/60$; Chlorine = $M/83$; Temp. = 32·6°.

Time in mins. ...	0	60	135	240	345	
$N/500$ Thiosulphate in c.c.	23·6	22·7	21·65	20·05	19·0	
Unimol. const. ...		·00028	·00028	·00030	·00027	Mean ·00028

The light reaction constant is thus 0·00022.

TABLE XV.

Experiment at 366·5μμ.

Cinnamic acid = $M/60$; Chlorine = $M/83$; Temp. = 32·6.

Time in mins. ...	0	57	152	252	
$N/500$ Thiosulphate in c.c.	23·45	22·5	21·3	19·8	
Unimol. const. ...		·00031	·00028	·00029	Mean ·00029

The constant in light is thus 0·00023.

Table XVI gives the temp. coefficients at different wave-lengths.

TABLE XVI.

Wave-length ...	436μμ	404μμ	366·5μμ
Temp. coefficient ...	$\frac{·00047}{·00034} = 1·38$	$\frac{·00022}{·00017} = 1·29$	$\frac{·00023}{·00021} = 1·10$

The temperature coefficient thus increases with increase in wavelength. This is in accordance with the ideas of Tolman (*J. Amer. Chem. Soc.*, 1923, **45**, 2285).

Influence of intensity on reaction rate.—The intensities of monochromatic radiation obtained by using filters being very small, influence of intensity could not be determined in monochromatic light as the reaction cell could not be pushed nearer. The influence of intensity was, therefore, determined by using white light. The reaction cell was placed at a distance of 17 cm. from the mercury lamp and a water filter of 4 cm. was employed as before. The incident intensity in this case was therefore half 144/289 the intensity in previous cases (Tables II-VII). Only two typical results are given below.

TABLE XVII.

Cinnamic acid = $M/30$; Chlorine = $M/86$; Temp. = 22·6°.

Time in mins. ...	0	25	55	85	
$N/500$ Thiosulphate in c.c.	23·1	20·4	17·8	15·3	
Unimol. const. ...		·0022	·0021	·0021	Mean ·0021

TABLE XVIII.

Cinnamic acid = $M/60$; Chlorine = $M/143$; Temp. = 22·6°.

Time in mins. ...	0	15	40	70	125	
$N/500$ Thiosulphate in c.c.	14·1	13·25	12·0	10·8	8·3	
Unimol. const. ...		·0018	·0018	·0017	·0016	Mean ·0017

Mean of the two series is 0·0019. The velocity constant with double this intensity (Tables II-VII) was 0·0039. The relative intensities in the two series of experiments were also measured by means of the Moll-thermopile using a 50 ohms resistance in series. With the mercury lamp at 12 cm., the deflection was 115 mm. and with the mercury lamp at 17 cm., the deflection was 64 divisions. The ratio of the intensities was thus 1·8. The ratio of the corresponding velocity contants is 2. The velocity constant is thus directly proportional to the intensity of light.

Theoretical.

The main features of the reaction are the following. The reaction is unimolecular with respect to chlorine and the velocity is unaffected by changes in the concentration of the acceptor so long as it does not fall too low. The quantum efficiency is greater than unity and gradually increases with increase in frequency. The problem now is to explain the observed facts.

The formation of excited chlorine molecules on absorption of light is not supported by experimental evidence. Bonhoeffer's experiment on the sensitisation of ozone decomposition by chlorine (*Z. Physik*, 1923, **13**, 94) and other experiments (*Physikal. Z.*, 1923, **24**, 504) indicate a long life of activated chlorine. One naturally expects fluorescence from excited molecules with a long life. Wood, and recently Kistiakowsky (*J. Amer. Chem. Soc.*, 1927, **49**, 2194) failed to observe fluorescence in gaseous chlorine. The present author also tried to detect fluorescence in carbon tetrachloride solutions of chlorine ($M/200$, $M/10$). Wood's method (*Phil. Mag.*, 1928, **6**, 729 for taking Raman spectra was employed. While the Raman lines due to carbon tetrachloride including the anti-Stokes lines appeared after half an hour's exposure, three hours' exposure failed to show any fluorescence band due to chlorine.

On the other hand Franck's hypothesis of dissociation of chlorine molecules by absorption of wave-length shorter than 4785A° is well supported by experiments. (Dymond, *Z. Physik*, 1925, **34**, 553 ; Kuhn, *Z. Physik*, 1926, **39**, 77). In the present case since the quantum efficiency is greater than unity, a chain reaction is indicated. We shall assume that the primary action of light is to dissociate the chlorine molecule into an excited and normal atom.

$$Cl_2 + h\nu \longrightarrow \quad Cl^* + Cl \qquad \ldots \quad (1)$$

Our experiments show that the rate of reaction is unaffected even when the cinnamic acid concentration falls low. This shows a long life of excited chlorine. It thus indicates that the reverse reaction $Cl^* + Cl = Cl_2$ is extremely slow in carbon tetrachloride. This is in accordance with the views of Kisiakowsky (*loc. cit.*) who explains the absence of Budde effect in dry chlorine by assuming that, in the absence of water vapour, the reaction $Cl^* + Cl \longrightarrow Cl_2$,

which gives rise to the heating effect, does not take place. In our experiments the carbon tetrachloride and chlorine were fairly dry and we take it, therefore, that the reverse reaction $Cl^* + Cl \rightarrow Cl_2$ does not take place. The concentration of excited chlorine atom is thus directly proportional to the light absorbed, *i.e.*, the intensity of incident light. We are thus able to explain why the unimolecular constant should be directly proportional to the intensity of light.

The excited Cl^* atom then combines with a cinnamic acid molecule to form the monochloride which carries the energy of excitation. Indicating a cinnamic acid molecule by *A*, the following reactions take place.

$$A + Cl^* \rightarrow ACl^* \quad \ldots \quad (2)$$

$$ACl^* + Cl_2 \rightarrow ACl_2 + Cl^* \quad \ldots \quad (3)$$

It is thus clear that the quantum efficiency should be greater than unity. The normal chlorine atom produced in (1) probably also forms *A*Cl (not activated) because of the unsaturated nature of cinnamic acid but the unexcited *A*Cl formed cannot produce a chain similar to reaction (3) and does not, therefore, increase the quantum yield per quantum. Such unactivated *A*Cl molecules will react in the following way.

$$ACl + ACl \rightarrow 2A + Cl_2 \quad \ldots \quad (4)$$

Why the quautum efficiency should increase with increase in frequency has got to be explained. It is known that a quantum of light of 478·5$\mu\mu$ is sufficient to dissociate the chlorine molecule. A quantum of higher frequency increases the kinetic energy of the excited chlorine atom and therefore, of the monochloride formed. If we assume that the length of the chain is proportional to the energy associated with the ACl^* formed, we can explain the increase in quantum efficiency with increase in frequency. The idea is similar to the concept of hot molecules of Christiansen and Kramers (*Z. physikal. Chem.*, 1923, **104**, 451).

Summary.

(1) The kinetics of the photochemical reaction between chlorine and cinnamic acid in carbon tetrachloride have been studied in white

light and also in monochromatic light. The reaction gives a unimolecular constant with respect to chlorine which is unaffected by changes in concentration of cinnamic acid and chlorine.

(2) The temperature coefficient is 1·1 at 366·5$\mu\mu$, 1·29 at 404$\mu\mu$, 1·38 at 436$\mu\mu$. The quantum efficiency is 2 at 436$\mu\mu$, 4 at 404$\mu\mu$ and 7 at 366·5$\mu\mu$. The following mechanism explains observed facts

$$Cl_2 + h\nu \longrightarrow Cl^* + Cl \quad \ldots \quad (1)$$

$$A + Cl^* \longrightarrow ACl^* \quad \ldots \quad (2)$$

$$ACl^* + Cl_2 \longrightarrow ACl_2 + Cl^* \quad \ldots \quad (3)$$

(3) An explanation is given for the increase in quantum effiiciency with increase in frequency.

(4) A solution of chlorine in carbon tetrachloride exhibited no fluorescence.

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A Note on Making Steel in a Basic Lined Converter from Indian Pig Iron at Mysore Iron & Steel Works.

By Prem N. Mathur.

Indian pig iron and consequently cast iron is unfit for either acid or basic standard practice.

Comparson of Analyses.

	T.C.	Si.	Mn.	S.	P.
American pig iron for acid practice.	3·50-4·25	1·0-2·0	·40-·80	·02-·07	Max..0·1
Continental pig iron for basic practice.	3·5-4·25	·2-1	·30-2·0	·02-·20	1·75-3·0
Indian pig iron reduced with charcoal or high phosphorus coke.	3·50-4·25	As desired.	As desired.	·03	·12-·40

The comparison of analyses clearly shows that due to high phosphorus, Indian pig iron is absolutely unsuitable for making steel in an acid converter, while in order to make pig iron suitable for the basic converter, we have to raise the phosphorus by at least 1·25%. This can only be accomplished either by adding ferro-phosphorus to the metal or phosphate rock to the blast furnace burden. High cost of ferro-phosphorus makes its addition absolutely prohibitive. So far the phosphate rock is not available in India in a sufficiently large quantity to warrant its use in the blast furnace in the manufacture of high phosphorus basic pig iron for basic Bessemer steel.

Practically all the foundries in India import acid pig iron from foreign countries at a great transportation cost. In India the steel castings are made by the acid converter, the electric furnace and the acid open-hearth processes. Consequently the cost of steel castings is very high. The result is that, whenever possible, some of the large users of steel castings in India have found it cheaper to import them from foreign countries rather than to buy them from Indian foundries.

Commercial steel in India for rolling and forging purposes is made by two processes, the open-hearth and the Duplex. In the open-hearth furnaces steel is made by melting a suitable mixture of steel scrap and pig ron, say in the ratio of 50:50 and removing the

impurities through the agency of ore, flame, mill scale, limestone, etc. In the Duplex process silicon, manganese and carbon are eliminated in an acid converter, while phosphorus is got rid of in a basic open-hearth furnace. Both these processes are far more expensive than the basic converter employed in Belgium and Germany to make cheap steel. The result is that Indian manufacturers have not been able to compete with foreign manufacturers who can afford to undersell their products in India.

Proposed new Method of Making Steel in India.

Depending upon the capacity of the converter, certain amount of cupola metal or direct blast furnace metal is collected in a ladle and then poured into the basic-lined converter to which a certain amount of burnt lime and mill scale have been previously added to neutralise the extra amount of silica formed from the oxidation of the silicon in the charge and at the same time produce highly oxidising basic slag, so essential for the removal of phosphorus. The blast is then applied and the metal blown as per standard acid practice. The main difference between this and the regular basic practice is that no afterblow is required for the oxidation and removal of phosphorus. The silicon and manganese contained in the charge produce high enough temperature for casting purposes. At the end of the blow the requisite amount of recarburisers and deoxidisers in the form of ferro-manganese and ferro-silicon are added to bring up the analysis to the required specification.

America and Europe have not considered the possibilities of the above-mentioned process, because the iron in the former country is sufficiently low in phosphorus while in the latter the iron is high enough in phosphorus for acid and basic practices respectively. Moreover, in Europe, the tendency is to use as high phosphorus pig iron as possible because they can employ the basic converter slag in the manufacture of agricultural fertilisers.

Author's successful Demonstration of the above Process at the Mysore Iron and Steel works, Bhadravati.

At the Mysore Iron Works they are making steel in a basic-lined baby converter, using direct charcoal blast furnace iron (·12% P) or cupola metal (·14-·15% P) and most successfully are reducing the phosphorus to ·026% in the best and ·066% in the worst blows.

The magnesite lining employed in basic converter has stood very well. No mill scale is used. In several heats even the addition of burnt lime has been omitted. The best results have been obtained with the following analysis.

Si	...	2·20%	S	...	·04%
Mn	...	·75%	P	...	·15%

The ingots forge very well. It is almost sure that even ·30 to ·40% phosphorus Indian acid pig iron can be blown successfully in a basic converter and phosphorus obtained within the Government specification for tinbar, mild steel, rail stock, etc., thereby effecting a great saving in the price per ton of steel manufactured in India in a basic converter using ordinary high phosphorus Indian pig iron. The silicon and manganese content of the metal used for blowing can be exactly the same as used for acid practice. As stated previously, the blow is handled similar to acid practice and absolutely no afterblow, whatsoever, is required.

Advantages of the Process.

(1) Making of cheap converter instead of costly electric or open-hearth furnace steel castings and ingots.

(2) Indian low phosphorus cast iron or pig iron made fit for basic blowing.

(3) No afterblow and consequently no danger of over-oxidising the metal.

(4) Small initial investment with high production at low cost.

(5) Independent of foreign costly acid pig iron for steel making, specially castings.

(6) Tremendous saving in steel ingots and castings made by this process as compared to other costly processes at present employed n the country.

TATA IRON AND STEEL CO., LTD.
JAMSHEDPUR.

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Coagulation of Colloidal Titanic Hydroxide.

By Subodh Kumar Majumdar.

The literature on the stability of positively charged hydrosols shows that though much work has been done on hydrosols of oxides of metals (*Ber.*, 1902, **35**, 4434; Samsonow, *Kolloid Z.*, 1911, **8**, 96) very little work has been carried out with the hydrosol of titanium oxide. In view of the fact that titanium oxide constitutes an important ingredient of the soil, the nature of whose reaction with different electrolytes at present forms a subject of considerable interest, a hydrosol of titanic oxide was prepared and its coagulation by several electrolytes as affected by ethyl and methyl alcohols, was investigated.

Experimental.

Equi-coagulating concentrations of different electrolytes were determined in the following manner (Mukherjee and Chaudhury, *J. Chem. Soc.*, 1924, **125**, 794): Equal volumes of the sol and the electrolyte were mixed in a dry Jena glass trough which was placed before an incandescent filament carrying a constant current. The times in which the sharp outline of the filament, as viewed through the trough, just disappeared, were noted for comparing the relative coagulating effects. Generally two readings had to be taken to note the exact point of disappearance especially when the time of coagulation was as small as 30 secs. It was found convenient to compare concentrations of electrolytes which produced this 'reference standard' of opalescence in 30 secs. The same colloid was used in each set of comparisons and the same procedure rigorously followed as it is well-known that slight variations, such as shaking or adding small quantities at a time, give totally different coagulating periods. (*Cp.* Freundlich, *Z. physikal. Chem.*, 1903, **44**, 129).

The colloid was prepared by taking conductivity water in a well washed parchment dialyser and carefully adding Kahlbaum's

chemically pure titanium chloride, drop by drop. After the fumes of hydrochloric acid had disappeared, the solution was dialysed for a fortnight, changing the dialysate every day. The precipitate produced on the first addition of the salt gradually passed into the colloidial state with time, until after a fortnight no precipitate was left at the bottom. At the end of the period, the dialysate did not show a greater turbidity with a solution of silver nitrate than tap water. During the course of any one set of experiments the colloid was tested from time to time with a particular strength of one electrolyte to detect changes in the coagulation time as defined above, resulting from ageing.

Sols A and B are different preparations. Sol C is a sample of sol B kept in a separate bottle and used after three months. The results are given in the following tables.

TABLE I.

Concentration of the sol : Titanium in 100 c.c. of the sol in terms of TiO_2 in gm.	Equi-coagulating concentrations in normality.					
	KCl	KBr	KNO_3	K_2SO_4	$K_4Fe(CN)_6$	$K_3Fe(CN)_6$
0·43 (Sol A)	0·5	0·75	0·6	0·016	0·0018	0·00057
0·23 (Sol B)	0·016	—	0·017	0·0019	0·00023	0·00019
0·23 (Sol C)	0·042	0·042	0·045	0·0027	0·00032	0·00025

TABLE II.

Concentration of the sol containing 0·23 gm. of TiO_2 in 100 c.c. of the sol.

P. c. of methyl alcohol.	Equicoagulating concentrations in normality :				
	KCl	KNO_3	K_2SO_4	$K_4Fe(CN)_6$	$K_3Fe(CN)_6$
0	·0167	·0176	·0019	·00023	·00019
2·5	·0154	·0176	·00174	·00022	·00019
5	·0147	·0176	·00166	·00022	·00019
10	·0141	·0176	·00158	·0002	·00019
25	·0131	·0176	·00143	·000178	·00021

TABLE III.

Sol B.

P. c. of ethyl alcohol.	Equicoagulating concentration in normality.				
	KCl	KNO_3	K_2SO_4	$K_4Fe(CN)_6$	$K_3Fe(CN)_6$
0	·0166	·0172	·0019	·00023	·000192
2·5	·0161	·0172	·0017	·0002	·000179
5	·0172	·0172	·00162	·0002	·000179
10	·0172	·0172	·00143	·000192	·00017
25	·0142	·0147	·0013	·000172	·00016

Discussion.

Table I shows that less of an electrolyte is necessary for coagulation, when the concentration of hydrosol is diminished. It is well-known that other hydroxide sols on dilution require smaller concentrations of electrolytes for coagulation. It is not possible however to enter into further discussions on the observed difference between the coagulation values of sols A and B in the absence of the measurement of the charge and the size of the particles. The coagulating capacities of the different anions are in the order: Ferri > Ferro > Sulphate > Chloride > Nitrate > Bromide, in conformity to the valency rule, and titanium hydroxide sol behaves as a typical positively charged hydrosol in this respect. The marked difference between the coagulating concentrations of all the electrolytes for sols B and C shows that, with time, changes take place in the sol which result in an increased stability. The nature of these changes requires further investigation. It may be remarked that the relative order of the coagulating concentrations of the different anions remains unchanged.

Tables II and III show that the hydrosol is sensitised by methyl and ethyl alcohols. The sensitising effect depends on the nature of the electrolyte. It will be noticed, however, that the coagulating concentration of potassium nitrate remains entirely unaffected in presence of even 25% methyl alcohol, whereas in the case of ethyl alcohol, it remains unaffected, up to 10%. But 25% of ethyl alcohol sensitises the sol towards potassium nitrate. Mukherjee, Chaudhury and Mukherjee (*J. Indian Chem. Soc.*, 1926, **3**, 349) have observed similar

behaviour with acids. Against potassium ferrocyanide, the sol is stabilised at higher percentages of methyl alcohol, whereas it is always sensitised in presence of ethyl alcohol. No satisfactory explanation of these observations is possible, and various reasons have been assigned to account for the effect of non-electrolytes by different authors that the effect of the non-electrolyte is specific and depends on its nature, as also on that of the electrolyte and the sol: the change in the coagulating concentration of the electrolyte is generally not very large. It is possible that the addition of a non-electrolyte produces mutually opposing effects as has been suggested by the above authors, so that the limits of variation in the coagulating concentration become small and in some cases the opposing effects neutralise each other. It is also possible that the explanation of coagulation is to be sought in a property of the electrolyte which is mainly determined by its nature and stoichiometric concentration (Mukherjee, Rai-Chaudhury and Bhattacharyya, *J. Indian Chem. Soc.*, 1928, **5**, 735), and that other factors such as activity of the ions and the dielectric constant and the changes in surface tension play a less important role.

Summary.

Titanium oxide hydrosol behaves as a typical positively charged hydrosol. The coagulating capacity of potassium salts is in the order: Ferri > Ferro > Sulphate > Chloride > Nitrate > Bromide and has been observed to remain unaffected by the quality or age for the samples used. The sol is sensitised in presence of methyl and ethyl alcohols towards the majority of electrolytes studied. On 'ageing' the sol becomes remarkably stable against coagulation by electrolyte.

My grateful thanks are due to Prof. J. N. Mukherjee for kindly providing me with facilities in his laboratory.

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The Extinction Coefficient of Br_3-ions and its Function in Photochemical Reactions.

By Rukmini Mohan Purakayastha.

It is a common fact that in the oxidation of many organic acids by bromine the velocity falls off rapidly with time. It is known that in such oxidation processes the negative ions of the acids are generally reactive. The rapid fall in the velocity is due to two factors. Firstly, hydrobromic acid which is one of the products of reaction throws back the dissociation of the reacting acid and secondly, the bromine ions of hydrobromic acid react with Br_2-molecules with the production of Br_3-ions which are quite inactive and hence the concentration of the effective bromine molecules is diminished.

If, in the beginning, sufficient HBr is added to maintain a fairly constant concentration of H^+ ions, and then varying amounts of potassium bromide are added, the reaction velocity is found to be proportional to the concentration of free bromine present at any instant, thus showing clearly that in dark reactions Br_3-ions are not at all reactive.

Many such reactions are also accelerated by light. The object of the present investigation was to find out if the function of the Br_3-ions is also the same in photochemical processes. Both bromine molecules and Br_3-ions being coloured it is obvious that the incident radiations will be shared between the two. It is possible that the light absorbed by Br_3-ions may in some way help the progress of the reaction or simply dissipate away.

Benrath (*Z. physikal. Chem.*, 1910, **74**, 115) has shown that in the oxidation of a tartaric acid by bromine in presence of an excess of HBr when the concentration of the acid is large in comparison to that of bromine, equal amounts of bromine are transformed in equal intervals. Even in absence of HBr, after some time when sufficient HBr accumulates in the system, the reaction becomes zero-molecular.

The same phenomenon has been observed in the oxidation of mandelic acid, lactic acid and some other organic acids by bromine in presence of a bromide. All these reactions follow the unimolecular

law in absence of any bromide. This behaviour must be obviously due to the influence of Br_3-ions.

In order to find out the function of Br_3-ions a knowledge of its extinction coefficient is essential. Since Br_3-ions only exist in solutions in equilibrium with Br_2-molecules, the method of determinations is obviously indirect.

The molecular extinction coefficient ϵ is given by the relation,

$$\epsilon = \frac{\log tan\ a_1 - \log tan\ a_2}{Cd}$$

where C and d are respectively the concentration of the substance and the depth of the absorption vessel, and a_1 and a_2 are the measure of the angles in positions 1 and 2 in a König-Marten spectrophotometer. From the known values of ϵ, C and d, the quantity (log *tan* a_1—log *tan* a_2) for any substance can be easily determined.

In the case of a solution containing Br_2 and KBr, the quantity (log *tan* am_1 − log *tan* am_2) will be due to the absorption of light by Br_2-molecules and Br_3-ions. From the equilibrium relation $Br^- + Br_2 \rightleftharpoons Br_3^-$ the concentration of free Br_2 and Br_3-ions in any mixture can be easily calculated.

If C be the total Br_2 concentration and C_1 be the concentration of free bromine molecules,

$$\log tan\ a_1 - \log tan\ a_2 = \epsilon_{Br_3} \cdot C_1 d$$

and

$$\epsilon_{Br_3} = \frac{(\log tan\ am_1 - \log tan\ am_2) - \epsilon_{Br_2} \cdot Cd}{(C - C_1)d}.$$

The quantities C, C_1 and d are known and ϵ_{Br_2} can be separately determined.

It is found that on the addition of a bromide to an aqueous solution of bromine, the red colour disappears and the solution becomes distinctly yellow. From this it can be inferred that Br_3-ions will have very little absorption in the yellow and green regions, and large absorption in blue and violet light. Experimental results also corroborate this.

Experimental.

The determination of am_1 and am_2 was made by means of a König-Marten spectrophotometer which was calibrated by means of a quartz mercury lamp. The source of illumination was a 500 c.p. "point-o-lite" lamp. Aqueous solutions of pure bromine and of bromine containing KBr were introduced into absorption vessels of different depths and a number of readings were taken for each solution. The mean of them gave am_1 and am_2. For the purpose of calculation of the concentrations of free Br_2 and Br_3-ions in the mixture, the value of K was taken to be 0 065 as given by Jakowkin (*Z. physikal. Chem.*, 1896, **20**, 19).

The following tables give the extinction coefficients of bromine molecules and Br_3-ions.

Table I.

Blue light—436$\mu\mu$.

Conc. of KBr.	Activity coeff.	Conc. of free bromine.	Conc. of Br_3-ion.	Depth of the absorption vessel.	log *tan* m_1 —log *tan* m_2.	ϵ.
0	—	·003365	—	4 cm.	·785	58·2
0	—	·002048	—	,,	·5065	61·8
0	—	·00161	—	,,	·3855	59·9
						Mean 60 = ϵ_{Br_2}
·2	·75	·00157	·00328	2 cm.	·8188	97·6
·1	·8	·00101	·001225	4	·6975	[93]
·0667	·83	·001495	·001235	2	·4351	104·0
·05	·84	·000625	·000405	4	·3273	109·4
·0333	·87	·000941	·000414	2	·2095	117·0
·02272	·9	·00061	·000175	4	·2242	111·0
						Mean 108 = ϵ_{Br_3}

TABLE II.

Green light—546 $\mu\mu$.

Conc. of KBr.	Activity coeff.	Conc. of free bromine.	Conc. of Br_3-ions.	Depth of the absorption vessel.	log *tan* m_1 —log *tan* m_2	ϵ.
0	—	·04125	—	2 cm.	·361	4·4
0	—	·04125	—	4	·72	4·45
0	—	·01924	—	4	·327	4·03
					Mean	4·3 = ϵ_{Br_2}
·125	·79	·01147	·015	4 cm.	·248	·80
·0833	·81	·01682	·01388	4	·3318	·76
·0833	·81	·01682	·01388	2	·1661	·81
·0416	·85	·02592	·0101	2	·237	·70
					Mean	·76 = ϵ_{Br_3}

TABLE III.

Yellow light—579$\mu\mu$.

0	—	·04125	—	2 cm.	·120	1·46
0	—	·04125	—	4	·2312	1·4
0	—	·01924	—	4	·1122	1·6
					Mean	1·5 = ϵ_{Br_2}
·2	·75	·00923	·01877	4 cm.	·0621	·09
·0416	·85	·02592	·0101	2	·0782	·02

Plotnikow (*Z. physikal. Chem.*, 1912, **79**, 357) gives the values of ϵ_{Br_2} as 59·5 for 436 $\mu\mu$, 4·52 for 546 $\mu\mu$ and 1·87 for 579 $\mu\mu$.

On account of very large absorption, measurements in the violet region could not be followed with the spectrophotometer. This was, however, done with a quartz spectrotgraph, the source of illumination being a copper arc, which showed that for all the radiations beyond 435$\mu\mu$, the extinction coefficient of Br_3-ions is much greater than that of Br_2.

The activity coefficients of KBr given in the above tables were taken from Lewis and Randall's "Thermodynamics."

It is seen from the results that Br_3-ions has practically no absorption in the yellow region while for green light it is much less than that

of Br_2. In blue and violet light its absorption is very high. On account of exceedingly small absorption, the measurements for the yellow region were erratic.

It has been already stated that the value of the constant K for the equilibrium $Br^- + Br_2 \rightleftharpoons Br_3^-$ has been taken to be 0·065. In a recent paper Hammick and others (*J. Chem. Soc.*, 1925, **127**, 2715) have shown that K has probably a higher value. Jakowkin's value 0·065 is for solution in which the concentration of bromine was in no case less than 0·04M and the electrotyles were assumed to be completely dissociated. His constants also show a tendency of regular increase with increasing dilution. In the reaction between formic acid and bromine by plotting the reciprocals of the monomolecular velocity constants against the Br-concentration Hammick and others (*loc. cit.*) obtained 0·07 as the value of K. The concentration of bromine in this case varied between 0·01M and 0·005M. The generally accepted value 0·065 is not far different from this. It is evident that if K has a higher value, the extinction coefficient of Br_3-ions for blue or violet light will be correspondingly higher. In these experiments in blue light the total concentration of Br_2 lies between ·001M and ·005M, and in green and yellow light between ·021M and ·035M. Assuming that K does change with dilution, in each region it may be regarded as fairly constant. It can be seen that if we choose 0·1, a much higher value for K for blue light with 0·2M -KBr and 0·00485M-Br_2, ϵ_{Br_3} changes from 97·6 to 103, and in the case of 0·05M-KBr and 0·00103M-Br_2, the change is from 109·4 to 124. So the relative variation is not much. The concentration of tribromide ion is always very low: so its activity may be regarded as equal to its concentration. The values of ϵ_{Br_3} given in the foregoing tables are not very concordant but, considering the method of determination involved and the uncertainty about the value of K, they may be regarded as fairly constant.

The Function of Br_3*-ions in Photochemical Reactions.*

For this purpose some reactions were studied which have no appreciable velocity in darkness. The solution of the reacting substances together with an aqueous solution of bromine containing different amounts of KBr was introduced into a reaction cell placed inside a double jacketted metal box and the temperature was kept constant by circulating water through the box by means of a pump.

The source of illumination was a "point-o-lite" lamp from which a parallel beam was obtained by means of a lens. The oxidation of mandelic acid and lactic acid was found to be quite suitable reactions because the dark reaction is negligible in comparison with the light reaction. The experimental results are given in the following tables. 2 C.c. of the reaction mixture were always titrated at regulur intervals with a standard thiosulphate solution.

TABLE IV.

Mandelic acid – 0·385*M*. Temperature—32°.

KBr – 0·2308*M*. Bromine – 0·00669*M*.

No light filter was used.

Time in mins. ...	0	15	30	46	60
$(a-x)$ ...	5·6	4·65	3·7	2·75	1·85
x/t ...	—	·0633	·0633	·0625	[·0607]

TABLE V.

Potassium bromide—0·462*M*.

Time in mins. ...	0	20	40	60	80
$(a-x)$ ...	5·65	4·8	3·95	3·15	2·35
x/t ...	—	·0425	·0425	·040	·040

TABLE VI.

Mandelic acid – 0·3846*M*.

Conc. of KBr.	Activity coeff.	Conc. of free Br_2.	Conc. of Br_3.	Free Br_2/Br_3.	x/t.
(1) ·1154	·79	·00285*M*	·003835*M*	·74	·114
(2) ·2308	·745	·00188*M*	·00485	·39	·0625
(3) ·2308	·745	·00325*M*	·00821	·4	·065
(4) ·4616	·7	·00114*M*	·00555	·2	·041
(5) ·4616	·7	·00226*M*	·00918	·25	·049
(6) ·23HBr		Total Br_2 ·0114*M*	—	—	·0575

TABLE VII.

Potassium bromide – 0·4615*M*. Bromine – 0·00669 *M*.

Conc. of mandelic acid.	x/t.	Ratio of conc. of the acid.	Ratio of velocity constant.
·2308	·029	From (1) and (2) – 1·67	1·45
·3846	·042	,, (2) and (3) – 1·4	1·4
·5385	·059	,, (1) and (3) – 2·33	2·03

It is evident from the results given in Table VI that as the ratio, free Br_2/Br_3 increases the velocity constant increases irrespective of the total amount of bromine present initially. It is also quite apparent that the rate of the reaction is not at all governed by the amount of free bromine present but it is in some way determined by the ratio, free Br_2/Br_3. Thus in experiments (4) and (5), the amount of free bromine varies as 1:2 but the velocity constants differ slightly because the ratios, free Br_2/Br_3 differ slightly. This is also evident from a comparison of the other results as well. Hydrobromic acid gives a slightly lower value because the dissociation of the reacting acid is diminished. Table VII shows that the velocity constants are nearly proportional to the concentration of mandelic acid.

The temperature coefficient of the reaction was found to be 1·7-1·8 which is given in the following table.

TABLE VIII.

Mandelic acid—0·3846*M*. Bromine—0·0114 *M*.

Temperature.	Conc. of bromide.	x/t.	Temp. coeff.
32°	·3846 KBr	·05	1·68
42°	·3846 ,,	·084	
32°	·23 HBr	·069	1·8
42°	·23 ,,	·108	

Mandelic acid—0·231*M*. Bromine—0·00669*M*.

32°	·4616 KBr	·029	1·7
42°	·4616 ,,	·05	

In order to test if the free bromine molecules are alone responsible for the reaction, some measurements were carried out in blue light for which the extinction coefficients of bromine molecules and Br_3-ions are known. The light filters used were the same as recommended by Plotnikow. The results of measurements are given in the following tables.

TABLE IX.

Blue light.

Mandelic acid—0·25*M*. Potassium bromide—0·15*M*. Bromine —0·0148*M*. Temperature—29·5°.

Time in minutes. ...	0	25	60	100	140
$(a-x)$ ...	7·4	6·7	5·75	4·65	3·55
x/t ...	—	·028	·027	·0275	·0275

TABLE X.

Potassium bromide—0·1*M*. Bromine—0·0104*M*.

Time in minutes. ...	0	25	50	75	100
$(a-x)$ ...	5·05	4·25	3·45	2·7	1·95
x/t ...	—	·032	·032	·030	030

TABLE XI.

Lactic acid—0·54*M*.

Potassium bromide—0·167*M*. Bromine—0·0267*M*.

Time in minutes. ...	0	25	50	85	115
$(a-x)$ ...	13·35	12·2	11·1	9·5	8·2
x/t ...	—	·046	·044	·045	·043

TABLE XII.

Potassium bromide—0·1*M*. Bromine—0·0154*M*.

Time in minutes ...	0	15	40	60	90
$(a-x)$ ...	7·7	6·9	5·55	4·45	2·95
x/t ...	—	·053	·054	·055	·050

A summary of the results is given in Tables XII and XIII.

TABLE XIII.

Blue light.

Mandelic acid—0·25*M*. Temp.—29·5°.

	Conc. of KBr.	Conc. of Br_2.	Conc. of free Br_2.	Conc. of Br_3.	x/t.	Energy absorbed in Hefners.	ψ*.	$\frac{x/t}{\sqrt{\psi I}}$.
A	·05	·042	·005395	·03255	·043	1·03	·56	·0565
B	·0833	·068	·00808	·00752	·037	1·15	·453	·051
C	·117	·0928	·00955	·01185	·0325	1·2	·37	·0487
D	·15	·116	·0056	·0092	·0256	1 16	·319	[·042]
E	·1	·08	·00485	·00556	·029	1	·4	·046
F	·0833	·068	·00803	·00752	·0183	·273	·453	·052
G	·05	·042	·005395	·003255	·0205	·25	·56	·055
H	·05	·042	·005395	·003255	·0122	·105	·56	·050

* $\psi = \dfrac{\text{Free bromine}}{\text{Free bromine} + Br_3 \times \frac{\epsilon_{Br_3}}{\epsilon_{Br_2}}}$

TABLE XIV.

Lactic acid—0·54*M*.

	Conc. of KBr.	Conc. of Br_2.	Conc. of free Br_2.	Conc. of free Br_3.	x/t.	Energy absorbed in Hefners.	ψ.	$\frac{x/t}{\sqrt{\psi I}}$.
I	·167	·128	·00985	·01685	·045	1·26	·31	·072
J	·1	·08	·0073	·0081	·054	1·14	·41	·079
K	·167	·128	·0093	·0163	·0245	·3	·305	·080
L	·1	·08	·0070	·0078	·029	·275	·408	·0865
M	·1	·08	·0070	·0078	·019	·127	·408	·083

The significance of the quantity $x/t/\sqrt{\psi I}$ will be explained later. It will be shown that this quantity should be a constant. The results given in the foregoing tables, however, show that there is a fairly large variation. For the calculation of $x/t/\sqrt{\psi I}$ the following measurements and assumptions had to be made.

(1) The value of k for the equilibrium $Br^- + Br_2 \rightleftharpoons Br_3^-$ was taken to be 0·065 for all the concentrations.

(2) ϵ_{Br_2} and ϵ_{Br_3} were determined separately and for the ratio $\epsilon_{Br_3}/\epsilon_{Br_2}$ a mean value of 1·3 was taken for the mean radiation 470$\mu\mu$ transmitted by the Plotnikow filters, after experimentally testing the ratio for a few rays.

(3) The amount of energy absorbed by the different solutions was determined separately.

As some error is always involved in such measurements, the values of $x/t/\sqrt{\psi I}$ may be regarded as fairly constant.

The results also make certain facts obvious. It will be seen from experiments A, B and C that the amount of total bromine as well as the amount of free bromine and also the energy absorbed is much greater in C than in B or A; but x/t has a larger value in A than in B or C. It is clear therefore that neither the amount of total bromine nor the amount of free bromine is the determining factor. It will be also seen that the ratios, free Br_2/Br_3 are approximately as 1·7, 1 and 0·8 in A, B and C respectively. That is the zeromolecular constant increases as the ratio, free Br_2/Br_3 increases.

The dark reaction in the case of bromine and lactic acid in presence of KBr is exceedingly small. In the case of mandelic acid, however, it is quite appreciable. 0·25M-mandelic acid, 0·05M-KBr and 0·009M-Br_2 gave a zeromolecular constant, 0·0035 at 29·5°. The dark reaction is, of course, unimolecular but for the convenience of calculation, it has been regarded here as zeromolecular; the error due to this is quite negligible. In all cases the dark reaction has been deducted from the values of x/t.

Oxidation of tartaric acid (Ghosh and Mukherjee, *J. Indian Chem. Soc.*, 1925, **2**, 165) and of mandelic acid, β-phenyl lactic acid and similar other hydroxy acids by bromine in absence of any bromide shows that these reactions have got a temperature coefficient between 1·7 and 1·8. The velocity constants vary as the square root of intensity and are very nearly proportional to the concentration of the reacting acids. A review of the results given in the foregoing tables will show that the same facts are observed in presence of a bromide. Consequently the mechanism of the reactions must be regarded to be the same in presence or in absence of any bromide. The kinetics of the reactions stated above have been studied both in light and in darkness in absence of any bromide and

will be shortly published. These reactions, however, show some peculiar phenomena, namely the existence of a well defined induction period and a considerable increase in the velocity with diminution in the concentration of bromine. These peculiarities disappear completely in presence of sufficient potassium bromide (Benrath, *Z. physikal. Chem.*, 1910, **74**, 115; Purakayastha, *J. Indian Chem. Soc.*, 1928, **5**, 721).

Discussion.

The experimental results recorded above bring out the following characteristics of the above photochemical reaction.

(1) That the reaction is zero-molecular in presence of excess of potassium bromide and the reacting organic acid.

(2) That the zero-molecular velocity constants increase as the ratio of free Br_2 : Br_3^- increases.

(3) That the velocity constant is proportional to the concentration of organic acid present in excess.

(4) That other experimental conditions remaining the same velocity constant is proportional to the square root of the intensity of incident blue light.

It appears that these observations can be quantitatively explained on the following hypothesis.

(*i*) Blue light absorbed by Br_3-ions is simply dissipated away as waste thermal energy and does not contribute in the least to the progress of the photo-bromination.

(*ii*) Blue light absorbed by free bromine molecules brings about a state of equilibrium as given below:

$$Br_2 + h\nu \rightleftharpoons 2Br,$$

the concentration of active bromine atoms being proportional to the square root of intensity of light absorbed by free bromine molecules alone.

If ϵ_1 be the molecular extinction coefficient of free bromine, and ϵ_2 the molecular extinction coefficient of Br_3-ions and if I be the intensity of incident blue light which is completely absorbed by the reacting solution or which remains constant during the progress of the reaction, it follows at once that the fraction of light absorbed by free bromine molecules is

$$\psi = \frac{\epsilon_1[Br_2]}{\epsilon_1[Br_2] + \epsilon_2[Br_3^-]}$$

or the intensity of light absorbed by free bromine molecules

$$\psi I = I\left[\frac{\epsilon_1[Br_2]}{\epsilon_1[Br_2]+\epsilon_2[Br_3^-]}\right]$$

It is apparent that in presence of excess of potassium bromide, the ratio $Br_2/Br_3 = K[Br] = \text{Const.}$

$$\text{or} \quad \frac{\epsilon_1[Br_2]}{\epsilon_2[Br_2]} = \text{Constant}, \quad \text{or} \quad \frac{\epsilon_1[Br_2]+\epsilon_2[Br_3]}{\epsilon_2[Br_3]} = \text{Constant},$$

$$\text{or } \psi = \text{Constant}.$$

That is, though during the progress of reaction, the absolute concentration of free bromine is continuously diminishing, the amount of light ψI absorbed by free bromine molecules alone remains the same throughout. Hence the concentration of active bromine atoms throughout the progress of photobromination $= K_1\sqrt{\psi I}$, and the velocity of reaction,

$$dx/dt = K_2.K_1\sqrt{\psi}\, I.C \qquad \ldots \quad (1)$$

where C is the concentration of reacting organic acid and K_2 the number of organic acid molecules reacted upon in a chain per each active atom of bromine produced. Since all the terms in the right hand side of the equation (1) are practically constant, $dx/dt = \text{constant}$. Hence the reaction is zeromolecular ;

$$\text{or} \qquad x/t = K\sqrt{\psi I}, \quad \text{or} \quad \frac{x/t}{\sqrt{\psi I}} = K.$$

In Tables XIII and XIV, the values of I, ψ and $x/t/\sqrt{\psi I}$ are given in columns 7, 8 and 9 respectively. It will be noticed that the values of $x/t/\psi I$ are fairly constant.

The increase in the values of x/t with the increase in the ratio free Br_2/Br_3 also makes it abundantly clear that the fraction of light absorbed by Br_2-molecules is alone photochemically active. We have, therefore, clear evidence of the fact that blue light absorbed by Br_3-ions becomes photochemically inert.

It should be mentioned here that the blue light obtained by using Plotnikow filters is not purely monochromatic. The filters also transmit a small amount of green and some other radiations, very

weekly absorbed by Br_2 and Br_3. It has been noticed that the blue light appears distinctly yellowish green after transmission through a Br_2 and KBr solution. We have also observed that when the concentration of KBr is small and the intensity of blue light is fairly high (as in expt. A, Table XIII), x/t slightly falls off with time but where the intensity is low or the concentrations of Br_2 and KBr are fairly high, there is absolutely no fall in the values of x/t. The intensity measurements given in column 7 (Tables XIII and XIV) also show that though the concentrations of Br_2 and KBr vary widely, there is only a 12-13% change in the amount of energy absorbed by the different mixtures, which is no doubt mostly due to the green rays. This does not however, mean that the amount of blue light does not remain constant during the progress of the reaction. This point has been thoroughly discussed by Ghosh and Purakayastha (*J. Indian Chem. Soc.*, 1927, **4**, 420). It has been shown that for blue light the variation in the amount of energy absorbed during the progress of the reaction when the final bromine concentration drops to a quarter of its initial value is negligible.

I am also of opinion that oxidation processes by iodine in presence of KI in light follow the same course. Some work in this direction is in progress.

Summary.

(1) The extinction coefficient of Br_3-ion has been determined for 536$\mu\mu$, 546$\mu\mu$ and 579$\mu\mu$.

(2) The oxidation of lactic and mandelic acids by bromine, which follows the unimolecular law, becomes zeromolecular in presence of a bromide in light.

(3) The zeromolecular constant increases with the free Br_2/Br_3.

(4) The experimental results have been satisfactorily explained on the assumption that only the fraction of light absorbed by bromine molecules is photochemically active, and the energy absorbed by Br_3-ions is photochemically inert.

I wish to express my gratitude to Prof. J. C. Ghosh for his kind interest and suggestions.

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Oxidation of Some Hydroxy Acids by Bromine. Part I. The Light Reaction.

By Rukmini Mohan Purakayastha.

The oxidation of tartaric acid by bromine was investigated by Ghosh and Mukherjee (*J. Indian Chem. Soc.*, 1925, **2**, 165), and by Ghosh and Basu (*ibid*, 1928, **5**, 343). They find that the reaction shows an induction period and also an after-effect and the velocity increases rapidly with diminution in concentration of bromine. The induction period was already noticed by Bunsen and Roscoe (*Pogg. Annalen*, 1857, **100**, 513 ; *Phil. Trans.*, 1857, **147**, 355, 601).

The problem which, however, is of peculiar interest is the enormous increase in the unimolecular velocity constant with diminution in concentration of bromine. Ghosh and Basu (*J. Indian Chem. Soc.*, 1925, **2**, 39) studied the oxidation of lactic acid by bromine but as they did it at only one concentration of the reactants, no information on the subject is available from their data.

Experimental.

The organic acids were all crystallised several times except lactic acid. Bromine was purified by distillation and freezing till of constant melting point. The lactic acid used was Merck's " very white extra pure " variety. In the preparation of the solutions conductivity water was always used.

The source of illumination was a 500 c.p. " point-o-lite " lamp and all the reactions were carried out in blue light using Plotnikow filters. The experimental arrangement is the same as described in other papers.

Table I.

Lactic acid $=0{\cdot}363M$. Bromine $=0{\cdot}01128M$. Temp. $=28{\cdot}5°$.

Time in minutes	...	0	40	65	72	80	90	109
$(a-x)$	...	13·7	11·9	9·0	7·6	6·1	4·75	3·55
k_1	...	Induction period		·0105	·0113	·0111	·0117	

TABLE II.

Lactic acid = 0·363*M*. Bromine = 0·0226*M*. Temp. = 28·5°.

Time in minutes	...	0	60	72	85	100	115	135
$(a-x)$	...	27·35	24·3	22·2	19·5	16·8	14·45	11·7
k_1	...	Induction period			·00434	·00432	·00432	·00442

TABLE III.

Mandelic acid = 0·31*M*. Bromine = 0·0232*M*. Temp. = 30°.

Time in minutes	...	0	10	25	38	45	52	59	71
$(a-x)$	...	30·2	28·0	25·1	20·4	16·4	13·0	10·6	7·4
k_1	...	Induction period			0135	·0140	·0135	·0133	

TABLE IV.

Mandelic acid = 0·31*M*. Bromine = 0·0114*M*. Temp. = 30°.

Time in minutes	...	0	20	30	35	40	45	50
$(a-x)$	...	15·0	12·1	8·5	5·85	4·1	2·75	1·7
k_1	...	Induction period			·0324	·0317	·0327	·0341

TABLE V.

Phenyl lactic acid = 0·08*M*. Bromine = 0·0056*M*. Temp. = 16°.

Time in minutes	...	0	10	26	30	37	51
$(a-x)$	...	8·15	7·6	6·8	4·8	3·9	2·65
k_1	...	Induction period			·0150	·0142	·0135

TABLE VI.

Citric acid = 0·253*M*. Bromine = 0·011*M*. Temp. = 22°.

Time in minutes	..	0	15	30	44	55	70
$(a-x)$	...	11·0	10·5	9·65	8·6	8·0	7·3
k_1	...	Induction period			·0028	·0029	·0028

In the following tables a summary of the experimental results is given.

TABLE VII.

Influence of the concentration of bromine.

Temp.	Concentration of acids.	Concentration of bromine.	k_1	Ratio of bromine concentration.	Inverse ratio of velocity constants.
28·5°	0·363 *M*-Lactic acid.	·0226*M*	·00435	2	2·5
		·01128*M*	·0111		
30°	0·31*M*-Mandelic acid.	·0232*M*	·0136	2·03	2·4
		·0114*M*	·0327		
22°	0·253*M*-Citric acid.	·0112*M*	·0041	2·03	2·2
		·0055*M*	·0088		
16°	0·08*M*-Phenyl lactic acid.	·0085*M*	·0078	1·5	1·75
		·0056*M*	·0132		

TABLE VIII.

Influence of concentration of the reacting acids.

emp.	Conc. of bromine.	Conc. of acids.	k_1.	Ratio of the concentration of acid.	Ratio of velocity constants.
28·5°	0·0226*M*	·533 *M*-Lactic acid.	·00607	1·47	1·35
	,,	·363 *M*- ,,	·00435		
	0·0118 *M*	·533 *M*- ,,	·0144	1·47	1·3
	0·0113 *M*	·363 *M*- ,,	·0111		
30°	0·0252 *M*	·31 *M*- Mandelic acid.	·0136	1·5	1·4
	,,	·465 *M*- ,,	·019		
16°	·0056 *M*	·68 *M*-Phenyl lactic acid.	·0132	1·6	1·4
	·00556 *M*	·05 *M* ,,	·0095		

TABLE IX.

Influence of intensity of incident light.

Temp.	Conc. of acids.	Conc. of bromine.	k_1.	Ratio of velocity constants.	Ratio of square root of intensity.
22°	0·46 *M*-Lactic acid.	·0188 *M*	·0167	1·46	1·6
	,,	·0186 *M*	·0245		
22°	0·253 *M*-Citric acid.	·011 *M*	·00283	1·45	1·5
	,,	·0112 *M*	·0041		
30°	0·31 *M*-Mandelic acid.	·0232 *M*	·0086	1·6	1·4
	,,	,,	·0136		
	,,	·0114 *M*	·0230	1·42	1·4
		·0112 *M*	·0327		

TABLE X.

Influence of temperature.

Temp.	Conc. of acid.	Conc. of bromine.	k_1.	Temp. coeff.
22°	·46 *M*-Lactic acid.	·0188 *M*	·0167	1·68
32°	,,	,,	·0284	
22°	·267 *M*-Mandelic acid.	·0152 *M*	·0174	1·8
32°	,,	,,	·0313	

The dark reaction in the case of phenyl lactic acid and bromine is quite considerable which is given in the following table.

TABLE XI.

Phenyl lactic acid=0·08 *M*. Bromine=0·00558 *M*. Temp.=16°.

Time in minutes	...	0	25	50	83	115	165	250
$(a-x)$	...	8·05	7·1	6·5	5·9	5·5	4·85	3·9
k_1	...		Initial	·00154	·00149	00123	·00119	·00115
							Mean	·00132

With the same concentration of bromine and the acid, k_1 has a value 0·0049 at 26° ; thus giving a high temperature coefficient of

3·9. The mean velocity constants due to the dark reactions have been deducted from the light reactions given in Table VII, IX and X. In the above table k_1 has been calculated by taking 7·1 as the initial reading because the induction period in the light reaction disappears when $(a-x)$ falls to near about this value.

TABLE XII.

Dark reaction.

Temperature—22°.

Mandelic acid = 0·235*M*. Bromine = 0·014*M*.

Time in hours. ...	0	·75	3	7	19·25	
$(a-x)$ ...	17·6	16·4	14·6	12·7	8·7	
Lactic acid = 0·239*M*.				Bromine = 0·139*M*.		
Time in hours. ...	0	·75	2·7	7·25	19·5	47
$(a-x)$ ...	17·4	17·0	16·7	16·0	14·4	10·8
Citric acid = ·232*M*.				Bromine = ·0139*M*.		
Time in hours. ...	0	·75	2·83	7·5	19·33	47
$(a-x)$ ...	17·85	16·9	16·5	15·7	14·1	12·1

It is evident that the velocity of dark reactions is small compared with light reaction and there is absolutely no induction period.

Application of Einstein's Law of Photochemical Equivalence.

It can be seen from the results that the velocity of the light reactions depends, to a large extent, on the concentration of bromine as well on the reacting acids. The reactions have a high temperature coefficient and also an induction period. So it is obvious that this law will not be applicable to these cases. For the sake of comparison, however, the number of quanta that bring about the transformation of a molecule of bromine in the case of each of these reactions is given in Table XIII. For the purpose of calculation, the quantity of bromine which disappeared in a certain interval after the period of induction was over, has been taken into consideration.

With 0·46*M*-lactic acid and 0·0188*M*-bromine, the change in the concentration of bromine was 0·01275*M* to 0·0055*M* in 21 mins.

The intensity of blue light just behind the reaction cell ($4\times4\times1$cm.) filled with water is $4·2/2·2\times900$ ergs. per sec. per sq.

cm., and when the same cell is filled with $0{\cdot}00912M$ (*i.e.*, $0{\cdot}01275—0{\cdot}0055/2M$) -bromine solution the intensity of light behind it is $1{\cdot}8/2{\cdot}2 \times 900$ ergs. per sec. per sq. cm.

$$\therefore \text{ The erergy absorbed is } \frac{(4{\cdot}2-1{\cdot}8)}{2{\cdot}2} \times 900 \text{ ergs.}$$

The number of quanta of blue light of average wave-length $470\mu\mu$ is

$$\frac{\frac{2{\cdot}4}{2{\cdot}2} \times 900 \times 470 \times 10^{-7}}{6{\cdot}5 \times 10^{27} \times 3 \times 10^{10}} = 2{\cdot}37 \times 10^{14}.$$

The number of molecules transformed

$$= \frac{(\cdot 01275 - \cdot 0055) \times 6{\cdot}1 \times 10^{27}}{21 \times 60 \times 1000} = 35{\cdot}1 \times 10^{14}.$$

$$\frac{\text{No. of mols. transformed}}{\text{No. of quanta absorbed}} = 15 \text{ (approx.).}$$

TABLE XIII.

Blue light of average wave-length $470\mu\mu$.

Temp.	Initial conc. of acid.	Initial conc. of bromine.	Amount of bromine transformed in gm. mols.	Time required for the transformation (mins.).	No. of quanta absorbed.	No. of mols. transformed.	No. of mols. / No. of quanta.
22°	$\cdot 46M$-Latic acid	$\cdot 0188M$	$\cdot 00725$	21	$2{\cdot}37 \times 10^{14}$	$35{\cdot}1 \times 10^{14}$	15
,,	$\cdot 265M$-Mandelic acid	$\cdot 0152M$	$\cdot 00685$	24	$2{\cdot}25 \times 10^{14}$	$29{\cdot}0 \times 10^{14}$	13
,,	$\cdot 253M$-Citric acid	$\cdot 011M$	$\cdot 00234$	40	$2{\cdot}25 \times 10^{14}$	$6{\cdot}75 \times 10^{14}$	3
16°	$\cdot 08M$-Phenyl lactic acid	$\cdot 0056M$	$\cdot 00243$	31	$\cdot 635 \times 10^{14}$	$8{\cdot}0 \times 10^{14}$	13

The reaction cell used in the reaction between bromine and phenyl lactic acid had the dimensions $4 \times 4 \times 2$ cm. and 3 c.c. of the reaction mixture were titrated each time, and in the case of other acids a $4 \times 4 \times 1$ cm. cell was used and the volume of reaction mixture titrated was 2 c.c.

From the foregoing tables it will be found that the velocity varies inversely as the concentration of bromine and is nearly proportional to the concentration of the acids. Calculation on this basis will make it evident that for a constant concentration of bromine and equimolecular concentrations of the acids, the number of molecules transformed per quantum of energy absorbed come out to be the largest in the case of phenyl lactic acid and smallest in the case of citric acid. Mandelic acid comes second and lactic acid third in order. It is quite interesting to see that the velocities of the dark reactions are also in the same order (Tables XI and XII).

Cassel (*Z. physikal. Chem.*, 1916. **92**, 113) also found a similar behaviour in the decomposition of chlor- and brom-acetic acids in ultraviolet light. Bromacetic acid has got a higher rate of decomposition both in light and in darkness.

Discussion.

Bromination and oxidation processes in which bromine takes part go to show that it is the bromine atom which is responsible for photochemical reactions. Experiments of Bodenstein and Berthoud also point to the same thing and in such reactions the velocity varies as the square root of the intensity of incident radiation. The first stage in the reaction is, therefore, the activation of bromine molecules by the absorption of light.

$$Br_2 + h\nu \longrightarrow 2Br \qquad \ldots \quad (1)$$

Ghosh and Basu (*J. Indian Chem. Soc.*, 1928, **5**, 343, 361) have suggested that the rapid rise in the velocity with diminution in concentration of bromine is due to the de-activation of the bromine atoms by collision with oxygen molecules present in the system in the dissolved state and also held in equilibrium due to the reaction,

$$2Br_2 + 2H_2O \rightleftarrows 4HBr + O_2 \qquad \ldots \quad (2)$$

It has been shown in a recent paper ((Purakayastha, *loc. cit.*) that this anomalous behaviour disappears in presence of a bromide or hydrobromic acid. It is easy to see that the amount of free bro-

mine in a solution containing sufficient bromide will be very small owing to the reaction,

$$Br_2 + Br^- \underset{\leftarrow}{\overset{\rightarrow}{\rightleftharpoons}} k_1 Br_3^- \qquad \ldots (3)$$

and also the rate of the reaction (2) will be exceedingly small due to the inertness of Br_3^--ions in darkness as well as in light. (A paper on the fuuction of Br_3^--ions in photochemical reactions appears in this issue of the *Journal*). The amount of oxygen due to reaction (2) will be much less in presence of HBr which, in addition, quite considerably increases the concentration of this component on the right hand side of equation (2). These facts, in a way, support the view put forward by Ghosh and Basu ; but it seems, probably this is not all. In a series of experiments with mandelic acid and bromine in presence of potassium bromide, the ratio, total Br_2/KBr was kept practically the same. The concentration of total bromine and free bromine varied from 0·0087 *M* to 0·0215 *M* and 0·0054 *M* to 0·0096 *M* respectively and the ratio, total Br_2/KBr was 1:5. As the concentration of total bromine as well as free bromine vary quite appreciably, it was expected that the velocity constants would increase with diminution in the concentration of bromine. The experimental results, however, show that the reaction velocity is solely determined by the ratio, free Br_2/Br_3^- quite irrespective of the concentration of total bromine or free bromine.

The experimental facts justify the assumption that the induction period is due to the formation of complexes by the interaction of the reactants or the existence of a solvent bromine complex. It should be stated in this connection that though the induction period disappears in presence of sufficient potassium bromide, it persists in presence of an equivalent concentration of hydrobromic acid. This leads to the view that probably a complex is formed by the interaction of bromine and the reacting acid. Hydrobromic acid increases the acid-bromine complex by throwing back the dissociation of the weak reacting acids whereas KBr may increase the ionisation and thus cause a further diminution in the concentration of the complex.

It has been found that the negative ions of the acids are reactive and a large number of molecules are transformed per quantum of energy absorbed. It is obvious, therefore, that the active bromine

atom is regenerated in the process. It is probable that an intermediate complex is formed by the reaction between the active bromine atoms and the negative ions of the acids which are subsequently oxidised by collision with bromine molecules with the liberation of the active bromine atoms.

Summary.

(1) The unimolecular velocity constants with respect to bromine are nearly proportional to the concentration of the reacting acids.

(2) The same constants vary nearly inversely as the concentration of bromine.

(3) The same constants vary as the square root of the intensity of incident radiation.

(4) The reactions have an induction period and also an after-effect. The after-effect in the case of mandelic acid and phenyl lactic acid was shown by Purakayastha (*J. Indian Chem. Soc.*, 1928, **5**, 721) and in the case of citric acid and lactic acid by Dhar and Mukerje (*ibid*, 1925, **2**, 277).

(5) The induction period disappears in presence of potassium bromide.

(6) A fairly large number of bromine molecules is transformed in each case, per quantum of energy absorbed.

I wish to express my gratitude to Prof. J. C. Ghosh for his suggestions and valuable advice.

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Oxidation of Some Hydroxy Acids by Bromine. Part II. The Dark Reaction.

By Rukmini Mohan Purakayastha.

It has been shown in Part I (previous paper) that citric acid and lactic acid react with bromine very slowly. The reaction between phenyl lactic acid and bromine is fairly large and that between mandelic acid and bromine is quite appreciable. In this paper an account of the influence of potassium bromide and some other electrolytes on the velocity of these reactions has been given. Somewhat similar reactions have been studied by Bugarsky (*Z. physikal. Chem.*, 1901, **38**, 561 ; 1904, **48**, 63) and by Hammick and others (*J. Chem. Soc.*, 1925, **127**, 2715).

It will be shown later that the negative ions of the acids are alone reactive and hence to study the mechanism of the reaction a constant hydrogen ion concentration must be maintained during its progress. This may be done by the addition of hydrochloric or hydrobromic acid. The diminution in the velocity in presence of the latter acid will be obviously much greater owing to the removal of bromine molecules as tribromide.

Table I.

Hydrobromic acid = 0·025*M*. Bromine = 0·0024*N*.

Phenyl lactic acid = ·05*M*. Temp. = 25°.

Time in mins. ...	0	60	100	150	260	400
$(a-x)$ ...	9·65	8·35	7·55	6·8	5·2	3·8
k_1		·00105	·00107	·00101	·00102	·00102

Table II.

Potassium bromide = 0·025*M*.

Time in mins. ...	0	30	90	140	230	300
$(a-x)$ ...	9·65	8·35	6·3	5·05	3·35	2·5
k_1		·00209	·00206	·00201	·00201	·00192

Table II shows that the reaction gives practically unimolecular constants in presence of sufficient bromide, thus showing that the rapid fall in the velocity is primarily due to Br-ions. It was thought that the influence of hydrogen ions could be very well studied by adding different amounts of hydrochloric acid ; but quite contrary and unusual results were, however, obtained. The velocity instead of being diminished increased quite considerably.

TABLE III.

Phenyl lactic acid = 0·05*M*. Temp. = 25°.

Conc. of HCl.	Initial conc. of bromine.	Final conc. of bromine.	Time required to reach the final conc.
0	·00238*N*	·00065*N*	150 mins.
·0062*M*	·00238	·000562	80
·0125	·00237	·000542	55
·025	·00236	·00054	30

TABLE IV.

·00625*N*-KCl	·0023*N*	·00054*N*	60 mins.
·0125*N*- ,,	·00224	·000545	35
·0125*N*-$BaCl_2$	·0023	·00053	30

It is evident that the increase in the velocity is much greater with potassium chloride than with the same concentration of hydrochloric acid. Similarly the retardation is much greater with HBr than with KBr (Tables I and II). This is due to the influence of hydrogen ions which throw back the dissociation of the reacting acid. Similar results were also obtained in the case of mandelic acid. In this case however, the velocity falls off quite appreciably even in presence of sufficient potassium bromide showing thereby that the influence of hydrogen ions must be also quite considerable. Table V gives the influence of different electrolytes on the velocity of this reaction.

TABLE V.

Mandelic acid = 0·25*M*. Temp. = 29°.

Conc. of electrolytes.	Initial conc. of bromine.	Final conc. of bromine.	Time required to reach the final conc.
0	·013*M*	·0044*M*	340 mins.
·0625*M*-KCl	·013	·0045	113
·125*M*- „	·0128	·0039	90
·1*M*-HCl	·0127	·0045	250
·15*M*-K_2SO_4	·0127	·0041	160

On the addition of gradually increasing amounts of NaOH to the reacting system which contains KBr, the velocity constant increases regularly. The alkali added forms an equivalent amount of sodium salt which completely ionises, and as the reaction velocity is found to be directly proportional to the amount of alkali added, the negative ions of the acids must be alone reactive. The amount of alkali added was always less than the concentration of the reacting acid so that the solution was always acid.

TABLE VI.

Potassium bromide = 0·05*M*. Caustic soda = 0·0375*M*.

Bromine = 0·0024*N*. Phenyl lactic acid = 0·05*M*. Temp. = 25°.

Time in minutes. ...	0	10	20	30	40	50	70
$(a-x)$ ...	10·5	7·8	5·9	4·45	3·4	2·7	1·6
k_1 ...	...	·0129	·0125	·0124	·0122	·0118	0·117

TABLE VII.

Conc. of NaOH.	k obs.	k obs./C_{NaOH}
·0125*N*	·00425	·336
·025	·00804	·322
·375	·0122	·325

The influence of Br-ions on the reaction might be accounted for by the removal of bromine molecules as tribromide ions, provided

that these do not take part in the reaction. In a solution containing a bromide and bromine

$$k_1 = [Br^-].\ [Br_2]/[Br_3^-] \quad \ldots \quad .1)$$

and $$(Br_2) = [Br_2] + [Br_3^-] \quad \ldots \quad (2)$$

where (Br_2) and $[Br_2]$ are the concentrations of total bromine and free bromine respectively. Combining (1) and (2) we have

$$[Br_2] = (Br_2)/[1 + [Br]/k_1] \quad \ldots \quad (3)$$

If the reaction is due to the free bromine molecules alone then the velocity should be proportional to their concentration at any instant and

$$k \text{ obs.} = k_2/[1 + [Br]/k_1] \quad \ldots \quad (4)$$

This conclusion was tested in the following way. The hydrogen ion concentration was maintained constant by the addition of sufficient HBr which also supplied the necessary minimum Br-ion concentration to give a monomolecular constant, and then the concentration of Br-ions was varied by the addition of potassium bromide.

TABLE VIII.

Hydrobromic acid = 0·024*M*. Temp. = 35°. Phenyl lactic acid = 0·046*M*. Bromine = 0·00204*M*.

Conc. of KBr.	Activity of KBr.	Total conc. of Br-ions.	*k* obs.	*k* obs. $[1 + [Br]/k_1]$
0	...	·019	·0036	·00458
·0192*N*	·0171	·0361	·0031	·0047
·0384	·0334	·052	·00264	·00456
·0768	·062	·081	·00209	·00454
·154	·119	·128	·00161	·00456
·308	·222	·241	·0011	·00484

Column 3 gives the total concentration of Br-ions due to hydrobromic acid and potassium bromide. The constancy of values in the last column is quite good. It has been also shown by us in a recent paper that Br_3-ions are also photochemically inert.

The influence of chlorine ions was also studied exactly in the same way. The concentration of chlorine ions was varied by the addition of potassium chloride.

TABLE IX.

Hydrobromic acid = 0·024*M*. Bromine = 0·00204*M*. Phenyl lactic acid = 0·046*M*. Temp. = 35°.

Conc. of KCl.	Activity of KCl.	*k* obs.	$k_1 - k$ obs.	$(k_1 - k \text{ obs.})/C_{cl}$.
0	—	·0036	—	—
·052*M*	·0437	·00612	·00282	·0645
·104	·0826	·00899	·00539	·065
·156	·12	·0118	·0082	·068

In the fourth column ($k_1 - k$ obs.) gives the increase in the unimolecular constant due to the corresponding chlorine ion concentration. The last column shows that the increase in the velocity constant is nearly proportional to the concentration of chlorine ions ; it has, however, a tendency to increase. Other negative ions also catalyse the reaction. Thus a 0·083*M* solution of potassium sulphate gave a velocity constant 0·00676. The increase in the velocity was found to be greater with barium chloride than with an equimolecular concentration of potassium chloride.

The activities of the electrolytes have been taken from Lewis and Randall's "Thermodynamics" (1923, p. 362) and the activities of HBr and KBr were regarded as the same as those of HCl and KCl respectively.

For the calculation of the constants given in column 5 (Table IX), k_1 was taken to be 0·07, which is not far different from the value 0·065 given by Jakowkin (*Z. physikal. Chem.*, 1896, **20**, 19) at 25°. Hammick and others (*loc. cit.*) consider the value of k_1 to be greater at higher solutions and obtain 0·07 as the value by plotting the reciprocals of the unimolecular velocity constants against the corresponding bromine ion concentrations. Jones and Hartmann (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 295) find k_1 to have a value 0·051 at 0°. From Worley's data (*J. Chem. Soc.*, 1905, **87**, 1107) at 26·5° and the value of k_1 at 0°, Linhart (*J. Amer. Chem. Soc.*, 1918, **40**, 158) calculates the value of k_1 and finds it to be equal to 0·064 at 32·6°,

which agrees very well with the value obtained from actual experimental data of Worley at the same temperature. In the present case the temperature of the experiments was 35°, so a slightly higher value 0·07 has been chosen. It should be said, however, that slight differences in the value of k_1 will not materially alter the constancy of the results.

A quantitative study of the influence of the various ions on the reaction between mandelic acid and bromine was not attempted. The velocity is very small in presence of HBr at ordinary temperatures. On the other hand at higher temperatures the loss of bromine due to evaporation will be quite considerable. Lactic acid and bromine did not show any noticeable change in the velocity in presence of a chloride.

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Changes in the Viscosity and Hydrogen Ion Concentration of some Inorganic Substances during the Process of Jelly Formation.

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In previous publications from these laboratories (*Z. anorg. Chem.*, 1926, **152**, 399 ; 1927, **164**, 63 ; 1927, **168**, 209) we have reported that jellies can be divided into three distinct groups. To the first group belong jellies of starch, gelatin, albumin, vanadium pentoxide, ceric hydroxide and blood clot. These jellies are, under suitable conditions, formed more or less instantaneously. Some of these jellies show the phenomenon of syneresis markedly. Jellies of iron, chromium and aluminium hydroxides belong to the second class and are probably formed by slow coagulation throughout he whole mass ; and von Weimarn jellies, as prepared from highly saturated solutions, belong to the third group. Moreover, our experimental results on viscosity measurements of colloids, especially of hydrophobic type, show that other things being identical, the uncharged substance is more hydrated than the sol, and greater the hydration of a substance, the greater will be its viscosity.

In order to throw light on the nature of jelly formation, we have measured the viscosity and hydrogen ion concentration during the process of gelation of several inorganic jellies. The viscosity measurements are recorded in the following tables.

Experimental.

Ferric hydroxide jelly.

Ferric chloride (4 c. c. of $M/2$) was mixed with ammonium sulphate (1 c. c. of $2M$), sodium acetate (2 c. c. of $3{\cdot}57N$) and water (12·5 c. c.). To the mixture was added ammonia (0·5 c. c. of $2{\cdot}34N$) with constant stirring till a clear solution was obtained. This solution sets to an opaque jelly in 6 hours. Viscosities were found out at different intervals by Farrow's method (*J. Chem. Soc.*, 1912, **101**, 347). Temperature was maintained at 30°.

TABLE I.

Time in minutes :	0	30	60	90	107	132
Viscosity :	0·009324	0·009324	0·009349	0·01158	0·01731	0·01928

When log of viscosity is plotted against time, a curve is obtained which shows that during the first portion of the graph, viscosity does not markedly change with time, but after two hours there is an abrupt rise in viscosity.

Chromium hydroxide jelly.

To 4 c. c. of *M*/2-chromic chloride, 8 c. c. of 3·57*N*-sodium acetate were added. After half an hour, 2 c. c. of 2*N*-ammonium sulphate and 6 c. c. of 2·34*N*-ammonia were added drop by drop and total volume was made up to 20 c. c. The mixture sets to a jelly in $6\frac{1}{2}$ hours. Viscosities were taken at 30°.

TABLE II.

Time in minutes :	0	30	60	90	120	150
Viscosity :	0·01465	0·01469	0·01527	0·01646	0·01873	0·02208

For the first two hours, there is very little change in viscosity but after that it varies exponentially with time, and during this period logarithms of viscosities plotted against time give almost a straight line. After five hours the mixture becomes highly viscous, and sets to a firm violet jelly in another hour.

Aluminium hydroxide jelly.

4 C. c. of *M*/2-aluminium nitrate were mixed with 2 c. c. of 3·7*N*-sodium acetate and 2 c. c. of 2*M*-ammonium sulphate. To the mixture, 1·3 c. c. of 2·34*N*-ammonia were added with constant stirring. Total volume was made up to 20 c. c. by adding requisite amount of water. This colourless solution sets to a white opaque jelly within $2\frac{1}{2}$ hours. Viscosities were determined at 30°.

TABLE III.

Time in minutes :	0	30	45	60
Viscosity :	0·009480	0·009480	0·009736	0·011580

After an hour the mixture becomes highly viscous, and sets in another 1½ hours. When logarithms of viscosities are plotted against time, the graph obtained is a curve.

Stannic hydroxide jelly.

20 C. c. of 1·43*M*-stannic chloride were mixed with 3 c. c. of 3·57*N*-sodium acetate, 1·7 c. c. of *M*-ammonium sulphate and 1·70 c. c. of 0·96 *N*-ammonia, total volume being 26·4 c. c. This colourless mixture sets to a firm white opaque jelly in the course of five hours. Viscosities were determined during the course of gelation at 30°.

TABLE IV.

Time in minutes :	0	15	30	45
Viscosity ;	0·009186	0·009298	0·009516	0·009788
Time in minutes :	60	78	98	120
Viscosity :	0·01031	0·0110	0·01352	0·02387

When logarithms of viscosities are plotted against time, a straight line is obtained, and thus viscosity changes exponentially with time.

Mercuric oxide jelly.

Bunce (*J. Phys. Chem.*, 1914, **18**, 269) obtained mercuric oxide jellies by mixing mercuric chloride solution with acetonic caustic potash. 20 C. c. of 6·4% mercuric chloride solution were gradually mixed with 20 c. c. of 0·807*N*-acetonic caustic potash solution which was prepared by dissolving about 22·5 gm. of caustic potash in 375 c. c. of water and 15 c. c. of acetone. The clear colourless solution sets to a white opaque jelly in 10 hours. Viscosities were determined at 30°.

TABLE V.

Time in minutes ;	0	17	30	50
Viscosity :	0·008483	0·008710	0·008910	0·009184
Time in minutes :	65	85	105	
Viscosity :	0·009828	0·01092	0·01486	

When logarithms of viscosities are plotted against time, a regular straight line is obtained in the beginning, but afterwards viscosities rise more abruptly.

Mercuri-sulphosalicylic acid jelly.

This jelly was obtained by dissolving freshly precipitated mercuric oxide (6·7 gm. HgO suspended in 100 c.c. of water) in 15·77% solution of sulphosalicylic acid. To 10 c.c. of sulphosalicylic acid were added 10 c.c. of water and 10 c.c. of mercuric oxide suspension. On stirring, a clear solution was obtained. This solution deposited a little precipitate during first five hours. This was filtered off and the clear filtrate set to a pinkish transparent jelly in 24 hours. Viscosities were recorded at 30°.

TABLE VI.

Time in hrs. & mins :	0	7/–	7/45	8/45
Viscosity :	0·008613	0·008972	0·009240	0·009290
Time in hrs. & mins. :	9/15	10/15	10/45	11/15
Viscosity :	0·009542	0·01209	0·01890	0·03483

After 11 hours the solution becomes highly viscous. There is no marked change in viscosity during first 6 hours. Then for another three hours, the graph obtained by plotting logarithms of viscosities against time is a straight line, but afterwards viscosities rise more abruptly.

Ferric arsenate jelly.

Grimaux (*Compt. rend.*, 1884, **98**, 1540), and Holmes (*J. Amer. Chem. Soc.*, 1916, **38**, 1970 ; 1919, **41**, 763) obtained a clear red jelly by dialysing solutions of ferric arsenate peptised by ferric chloride. 100 C.c. of about 1·5 *N*-solution of ferric chloride were mixed with 40 c.c. of 18% potassium arsenate solution, and the mixture was dialysed for 4 days. The sol on heating in a platinum crucible gave 44·8 gm. Fe_2O_3/ litre.

To 30 c.c. of this ferric arsenate sol were added 3·75 c.c. of *N*/10-potassium sulphate. This mixture sets to a firm transparent red jelly in course of 4 days. Viscosities were taken at 30°.

TABLE VII.

Time in hrs. & mins :	0	0/26	0/56	1/23	2/0
Viscosity :	0·01507	0·01540	0·01603	0·01664	0·01689
Time in hrs. & mins. :	2/28	3/0	22/26	23/30	26/10	72/0
Viscosity :	0·01719	0·01746	0·02620	0·02682	0·02863	0·1049

When logarithms of viscosities are plotted against time, a regular straight line is obtained from the very beginning and is maintained for a long interval of time.

Ferric phosphate jelly.

Holmes (*J. Amer. Chem. Soc.*, 1916, **38**, 1970) has observed that when a sol obtained by peptising ferric phosphate with ferric chloride is dialysed, a red transparent gel is obtained. We have obtained a clear sol by dialysing a mixture of $M/2$-ferric chloride solution, and 22% potassium phosphate (KH_2PO_4) solution in ratio of 2 to 1 by volume, which sets to a red clear jelly on addition of potassium sulphate. 15 C.c. of the sol containing 46 gm. of ferric phosphate per litre, were mixed with 1·2 c.c. of $N/4$-potassium sulphate. Viscosities were taken at 30°.

TABLE VIII.

Time in minutes :	0	40	80	130	185	252
Viscosity :	0·01859	0·02159	0·02648	0·03176	0·03876	0·04997

After five hours, the sol becomes very viscous, though it completely sets in 36 hours. When logarithms of viscosities are plotted against time, a straight line is obtained, showing that viscosity is varying exponentially with time.

Ferric molybdate jelly.

We have observed that when potassium molybdate solution is added to ferric chloride solution, a precipitate is obtained which disappears on shaking. If this clear solution be allowed to stand, it develops opalescence, and finally an opaque yellow gel is obtained. To 8 c.c. of $M/2{\cdot}69$-ferric chloride solution were added 4 c.c. of water and 8 c.c. of 10% potassium molybdate solution. The mixture sets to a gel in 10 hours. Viscosities were taken at 30°.

TABLE IX.

Time in minutes :	0	15	32	46	68
Viscosity :	0·009966	0·01009	0·01029	0·01052	0·01094
Time in minutes :	98	128	158	188	300
Viscosity :	0·01233	0·01442	0·01916	0·03526	0·10620

When logarithms of viscosities are plotted against time, an interesting curve is obtained. The first portion of the curve (up to 68 minutes) is a straight line with less slope. Then for another one and half hours, another straight line of a deeper slope is obtained. In the third portion of the curve, viscosity changes are more abrupt.

Chromium arsenate jelly.

Holmes (*J. Amer. Chem. Soc.*, 1916, **38**, 1980) observed that a colloidal solution of chromium arsenate, peptised by chromic chloride, sets to a firm green transparent jelly on continued dialysis. We prepared a clear sol by adding 1 part by volume of 18% potassium arsenate solution to 3 parts of about $M/2$-chromic chloride solution, and dialysing it for 5 days. The sol contained 35 gm. Cr_2O_3 per litre. 20 C.c. of this sol were mixed with 2 c.c. of $N/100$ -potassium sulphate which sets to a clear jelly in three days.

TABLE X.

Time in hrs. & mins :	1/0	1/44	2/29	3/20	4/16	46/-
Viscosity :	0·02551	0·02740	0·02945	0·03267	0·03595	0·6080

The change in viscosity with time is fairly exponential for sufficient interval. The graph obtained by plotting logarithms of viscosity against time for the first five hours is a straight line.

Stannic tungstate jelly.

8 C.c. of stannic chloride solution (1·35 M) were mixed with 2 c.c. of water and 14 c.c. of 15% sodium tungstate solution. The mixture sets to a firm white jelly in the course of 10 hours. Viscosities were taken at 30°.

TABLE XI.

Time in mins :	0	90	125	168	210	245	283
Viscosity :	0·01349	0·01570	0·01640	0·01691	0·01807	0·02015	0·02230

The graph obtained by plotting logarithms of viscosities against time is a straight line for first four hours and then viscosities rise more abruptly.

Stannic molybdate jelly.

1·5*M*-stannic chloride solution was mixed with 25% potassium molybdate solution below the precipitation value and the mixture was allowed to dialyse for two days. A clear transparent sol was obtained. With 5 c.c. of this sol were mixed 5 c.c. of water. The mixture sets to a jelly within 5 hours. Concentration of the sol =91·04 gm. SnO_2/ litre.

Change in viscosity during gelation was recorded by Ostwald's viscosimeter at 25°. Viscosity of water at 25° is 0·00893.

TABLE XII.

Time in minutes :	0	3	5	10	20
Viscosity :	0·01272	0·01353	0·01471	0·01804	0·02300
Time in minutes :	30	40	60	80	
Viscosity :	0·03032	0·03447	0·04412	0·07505	

When logarithms of viscosities are plotted against time, a straight line is obtained. After one and half hours, the sol becomes highly viscous.

Ferric borate jelly.

To *M*/2·69-ferric chloride solution, a saturated solution of borax was added below the precipitation point with constant stirring. A red clear sol was obtained after dialysing the solution for 30 days. The sol contained 11·78 gm. of ferric borate per litre. To 18 c.c. of this sol, 1·4 c.c. of water and 0·6 c.c. of *N*/10-potassium chloride were added and viscosities were taken during gelation. The mixture sets to a jelly in 8 hours. Viscosities were recorded by Farrow's method at 30°.

TABLE XIII.

Time in minutes :	0	23	56	90
Viscosity :	0·01210	0·01559	0·02072	0·02720

The graph obtained by plotting logarithms of viscosity against time is a straight line.

Thorium phosphate jelly.

To 10 c.c. of thorium nitrate solution (12·035 g. in 250 c.c) were added 1·6 c.c. of 22% potassium phosphate solution and the mixture

was well-shaken. The solution becomes very viscous within a short period. Viscosities were measured by Ostwald's viscosimeter at 25°.

Time of flow for water at 25° = 99 seconds, and viscosity of water at 25° = 0·00899.

TABLE XIV.

Time in minutes.	Time of flow.	Viscosity.
0	375 seconds.	0·03383
9	988 seconds.	0 08914
27	More than 2½ hours.	—

The mixture sets to a transparent jelly in 6 hours.

Thorium molybdate jelly.

10 C. c. of thorium nitrate solution (12·035 gm. in 250 c.c.) were mixed with 0·8 c.c. of water and 1·2 c.c. of 3% potassium molybdate solution. The mixture sets to a transparent jelly in 23 hours, though it becomes highly viscous within one hour. Viscosities were measured by Ostwald's viscosimeter at 25°.

TABLE XV.

Time in minutes :	0	5	9	15	25
Viscosity :	0·02030	0·02517	0·02950	0·03915	0·05170
Time in minutes :	40	55	79		
Viscosity :	0·07560	0·11840	0·25960		

The graph obtained by plotting logarithms of viscosities against time is fairly a straight line for a sufficient period.

Thorium arsenate jelly.

10 C.c. of thorium nitrate solution (12·035 gms. in 250 c.c.) were mixed with 0·65 c.c. of 18% potassium arsenate solution and 1·35 c.c. of water. The mixture sets to a transparent jelly with slight opalescence in 3 hours. Viscosities were measured by Ostwald's viscosimeter at 30°.

TABLE XVI.

Time in minutes :	0	15	40	60	70
Viscosity :	0·008806	0·009670	0·01088	0·01442	0·01770
Time in minutes :	80	90	100	120	140
Viscosity :	0·02253	0·026253	0·03022	0·03902	0·11920

When logarithms of viscosities are plotted against time, the graph is a straight line between the first and second hours. There is very little change in the viscosity in the beginning, while in the third hour the viscosity changes abruptly.

Our results on viscosity measurements generally show three stages in gelation :

(*i*) In the first stage, there is very little change in viscosity with time.

(*ii*) In the second stage, there is regular exponential change with time.

(*iii*) In the third stage, viscosity goes on increasing abruptly till a jelly is formed.

The first stage corresponds to the region when true electrolytic solution passes to the colloidal condition, *i.e.*, colloidal condition is not at once attained after mixing the solutions, and it takes some time during which period there is very little change in viscosity. Jellies of iron, chromium, and aluminium hydroxides as well as that of mercuri-sulphosalicylic acid exhibit this stage markedly.

In the second stage, the mixture has attained colloidal condition, and there is regular exponential change in viscosity due to the gradual charge neutralisation and thus increase in hydration. Dialysed sols of chromium arsenate, ferric arsenate, phosphate and borate, and stannic molybdate do not show the first stage because here we initially start with the colloids obtained by dialysis, and the addition of slight trace of coagulating electrolyte, from the very beginning, causes regular decrease in charge and corresponding increase in hydration. Thus in these jellies, viscosities vary strictly exponentially for a great length of time, and fair straight lines are obtained when values for logarithms of viscosities are plotted against time. At the end of the second stage, viscosity changes are more abrupt, and there is a sudden rise in the curve. This stage is really where the formation of specific structure of jellies takes place. Sometimes the second

and the third stages are mixed up, and in these cases a regular curve is obtained—as in the case of iron and aluminium hydroxides—even when logarithms of viscosities are plotted against time. Kugelmass ("Colloid Symposium Monograph", 1925, **3**, 195) has studied the changes in viscosity in the course of coagulation or clotting of blood. The viscosity was found to increase very slowly at first, then at the point of clot indication vary rapidly till a maximum was reached.

The changes in hydrogen ion concentration during gelation are recorded below.

Ferric hydroxide jelly.

In the case of iron and some other jellies, the use of quinhydrone electrode was found more suitable than Hildebrand's hydrogen electrode. The jelly-forming solution was mixed with a little quinhydrone (about 50-100 mg.) and the electrode used was a bright piece of platinum foil. The electromotive force developed against a *N*-KCl/calomel electrode was measured by vernier potentiometer (Scientific Instrument Co., Cambridge). The following expression of Kolthoff (*Z. physiol. Chem.*, 1925, **144**, 259) was used for the calculation of p_H values.

$$p_H = \frac{0{\cdot}4181 - 0{\cdot}0005(t-18) - E}{0{\cdot}0577 + 0{\cdot}0002\ (t-18)}$$

where t is the temperature and E, the electromotive force developed against *N*-KCl/calomel electrode.

The following solutions were mixed as in the viscosity experiments:—

M/2-Ferric chloride	...	6 c.c.
2·84 *N*-Sodium acetate	...	3·75 c.c.
2*M*-Ammonium sulphate	...	1·5 c.c.
4·26 *N*-Ammonia	...	0·45 c.c.
Total volume	...	30 c.c.
Time for gelation	...	6 hours.

TABLE XVII.

Time in mins.	E. M. F.	p_H	c_H	Dimiuution in c_H.	% Dimunition in c_H.
0	0·248	2·91	$1{\cdot}23 \times 10^{-3}$		
15	0·239	3·06	0·87 ,,		
30	0·230	3·22	0·602 ,,		
45	0·228	3·26	0·549 ,,	$0{\cdot}681 \times 10^{-3}$	55·3
60	0·228	3·26	0·549 ,,		
120	0·228	3·26	0·549 ,,		

Chromium hydroxide jelly.

M/2-Chromium chloride	...	4 c.c.
3·57 *N*-Sodium acetate	...	8 c.c.
2*M*-Ammonium sulphate	...	2 c.c.
2·34 *N*-ammonia	...	6 c.c.
Total volume	...	20 c.c.
Time for jelly formation	...	7 hours.

TABLE XVIII.

Hydrogen electrode and *N*-KCl/calomel electrode were used.

Time in mins.	E. M. F.	p_H	c_H	Diminution in c_H.	% Diminution in c_H.
0	0·578	4·96	$1·096 \times 10^{-5}$		
5	0·597	5·28	5·25 ,,		
30	0·599	5·31	0·490 ,,	$0·615 \times 10^{-5}$	56·6
45	0·599	5·31	0 490 ,,		
180	0·5996	5·32	0·479 ,,		

Aluminium hydroxide jelly.

M/2-Aluminium nitrate	...	4 c.c.
2*M*-Ammonium sulphate	...	2 c.c.
3·57 *N*-Sodium acetate	...	2 c.c.
2·34 *N*-Ammonia	...	1·3 c.c.
Total volume	...	20 c.c.
Time for jelly formation	...	3 hours.

TABLE XIX.

Hydrogen electrode and *N*-KCl/calomel electrode were used.

Time in mins.	E. M. F.	p_H	c_H	Diminution in c_H	% Diminution in c_H.
0	0·4670	3·082	$0·828 \times 10^{-3}$		
30	0·4950	3·550	0·282 ,		
45	0·510	3·810	0·155 ,,	$0·673 \times 10^{-3}$	81
60	0·510	3·810	0·155 ,		
75	0·510	3·810	0·155 ,,		

Ferric molybdate jelly.

M/2 Ferric chloride	... 10 c.c.
10% Potassium molybdate	... 8 c.c.
Water	... 2 c.c.
Time for jelly formation	... 7 hours.

Quinhydrone and *N*-KCl/calomel electrodes were used.

TABLE XX.

Time in minutes.	E.M.F.	p_H	c_H	Diminution in c_H.	% Diminution in c_H.
0	0·115	5·20	$6·31 \times 10^{-6}$		
10	0·095	5·54	$2·89 \times 10^{-6}$	$4·12 \times 10^{-6}$	65·3
30	0·088	5·66	$2·19 \times 10^{-6}$		
60	0·088	5·66	$2·19 \times 10^{-6}$		

Thorium arsenate jelly.

Thorium nitrate, 12·035 gm./250 c.c.	... 10 c.c.
Potassium arsenate, 18% solution	... 0·4 c.c.
Water	... 1·6 c.c.
Time of jelly formation	... 3 hours.

Quinhydrone and *N*-KCl/calomel electrodes were used.

TABLE XXI.

Time in minutes.	E M.F.	p_H	c_H	Diminution in c_H.	% Diminution in c_H.
0	0 341	1·31	$0·490 \times 10^{-1}$		
10	0·340	1·33	$0·468 \times 10^{-1}$		
20	0·339	1·34	$0·457 \times 10^{-1}$	$0·054 \times 10^{-1}$	11
30	0·338	1·36	$0·436 \times 10^{-1}$		
60	0·338	1·36	$0·436 \times 10^{-1}$		

Thorium phosphate jelly.

Thorium nitrate, 12·035 gm./250 c.c.	...	10 c.c.
Potassium phosphate, 22% solution	...	0·5 c.c.
Water	...	1·5 c.c.
Time for gelation	...	3 hours.

Quinhydrone and *N*-KCl/calomel electrodes were used.

TABLE XXII.

Time in minutes.	E.M.F.	p_H	c_H	Diminution in c_H.	% Diminution in c_H.
0	0·343	1·27	$0·537 \times 10^{-1}$		
10	0·3395	1·33	0·468 ,,		
20	0·3375	1·37	0·426 ,,	$0·121 \times 10^{-1}$	22·4
30	0·3370	1·38	0·416 ,,		
60	0·3370	1·38	0 416 ,,		

Thorium molybdate jelly.

Thorium nitrate, 12·035 gms./250 c.c.	...	10 c.c.
Potassium molybdate, 3% solution	...	2 c.c.
Time for jelly formation	...	5½ hours.

Quinhydrone and *N*-KCl/calomel electrodes were used.

TABLE XXIII.

Time in minutes.	E.M.F.	p_H	c_H	Diminution in c_H.	% Diminution in c_H.
0	0·291	2·16	$0·692 \times 10^{-2}$		
20	0·283	2·30	0·501 ,,		
35	0·280	2·34	0·457 ,,	$0·285 \times 10^{-2}$	41·2
45	0·2792	2·37	0·427 ,,		
70	0·282	2·39	0·407 ,,		
80	0·282	2·39	0·407 ,,		

Stannic tungstate jelly.

$M/1{\cdot}099$-Stannic chloride	...	10 c.c.
10% Sodium tungstate solution	...	10 c.c.
Time for jelly formation	...	10 hours.

Hydrogen electrode and N/10-KCl/calomel electrode were used.

TABLE XXIV.

Time in minutes.	E.M.F.	p_H	c_H	Diminution in c_H.	% Diminution in c_H.
0	0·3896	0·907	$1{\cdot}24 \times 10^{-1}$		
5	0·3344	0·988	1·03 ,,		
10	0·3964	1·021	0·953 ,,	$0{\cdot}379 \times 10^{-1}$	32·6
20	0·3980	1·049	0·893 ,,		
30	0·3990	1·065	0·861 ,,		
60	0·3990	1·065	0·861 ,,		

Stannic phosphate jelly.

$M/1{\cdot}048$-Stannic chloride	...	10 c.c.
22% Potassium phosphate	...	6·6 c.c.
Total volume	...	20 c.c.
Time of gelation	...	2 hours.

Hydrogen electrode and N-KCl/calomel electrode were used.

TABLE XXV.

Time in minutes.	E.M.F.	p_H	c_H	Diminution in c_H.	% Diminution in c_H.
0	0·2990	0·240	$5{\cdot}75 \times 10^{-1}$		
7	0·3003	0·262	5·47 ,,	$2{\cdot}17 \times 10^{-1}$	37·7
30	0·3112	0·446	3·58 ,,		
50	0·3112	0·446	3·58 ,,		

Stannic arsenate jelly.

$M/1{\cdot}048$-Stannic chloride	...	10 c.c.
18% Potassium arsenate solution	...	10 c.c.
Time of gelation	...	1 hour.

TABLE XXVI.

Hydrogen electrode and N/KCl-calomel electrode were used.

Time in minutes.	E.M.F.	p_H	c_H	Diminution in c_H.	% Diminution in c_H.
0	0·2297	0·220	$6{\cdot}03 \times 10^{-1}$		
10	0·300	0·257	5·54 ,,	$0{\cdot}49 \times 10^{-1}$	8
30	0·300	0·257	5·54 ,,		

The foregoing results show that in many cases there is considerable decrease in the hydrogen ion concentration on gelation. In some cases the decrease comes up to 50% of the original hydrogen ion concentration. It has been observed by Kugelmass (*loc. cit.*, p. 160) that during blood clotting the hydrogen ion concentration changes continuously, and the rate of diminution of hydrogen ion concentration is great at the first interval but it gradually falls off approaching zero, *i.e.*, an asymptotic limit. It has been also observed that the higher the initial hydrogen ion concentration, the greater the diminution in c_H after clotting. By starting with solutions of different initial hydrogen ion concentrations, the diminution in hydrogen ions was found to be 50 ± 10. Our results give average diminution in most cases to be 50 ± 20. The influence of hydrogen ions on the formation of jellies has been studied by Kraemer ("Colloid Symposium," Wisconsin, 1923, **1**, 62) in the case of manganese arsenate jellies. Tarr (*Dela. agri. expt. sta. Bull.*, 1923, **134**, Tech. 2) has observed that for minimum point of jelly formation, p_H 3·40 must be obtained whether mineral or organic acids are used in preparation of fruit jellies if pectin and sugar contents are kept constant.

According to the transparency, jellies may be divided into three classes:—

(*a*) Perfectly transparent jellies, which retain their transparency for a long time, *e.g.*, arsenates of zinc, manganese, iron(*ic*), chromium

and thorium ; phosphates of iron and thorium ; and other jellies as of mercuri-sulphosalicylic acid.

(*b*) Transparent jellies with some opalescence at the point of setting, but opacity increasing with time, and finally during the course of a few hours forming perfectly opaque firm jellies, *e.g.*, stannic tungstate, borate, phosphate, molybdate and arsenate jellies.

(*c*) Clear sols, developing opalescence and finally, at the point of setting, they become perfectly opaque, *e.g.*, ferric molybdate, ferric tungstate, hydroxides of iron, tin, aluminium and chromium.

Von Weimarn jellies which are precipitated from the highly concentrated solutions are also transparent in the beginning, but after a few minutes, they become perfectly opaque. From the transparency of jellies, it may be concluded that the process of gelation is accompanied by (*i*) increase in the hydration or the adsorption of the solvent, and (*ii*) the growth of particles. When the first factor is alone taking part in gelation, transparent jellies are obtained. For example, when some coagulating electrolyte such as potassium sulphate is added to ferric arsenate sol charge neutralisation begins, but the same forces which bring out the agglomeration of these uncharged particles cause them to adsorb the solvent medium, and thus, instead of precipitation, jelly elements are formed which may give rise to either gelatinous precipitates (if the coagulating electrolyte is in excess) or jellies under suitable conditions. These jellies are perfectly transparent.

In case of jellies of second class, growth of particles begins after the setting of jellies. Some of the residual forces, which remain after hydration and adsorption of solvent, bring out the agglomeration of some particles after gelation and thus, finally, perfectly opaque jelly is formed.

In other jellies where sol develops opacity from the very beginning before setting, growth of particles and hydration tendency develop side by side, and only opaque jellies are obtained. These jellies have the weakest texture while the jellies of the first class are most firm.

Thus, on neutralisation of the charge, the tendency of particles is either to agglomerate or to hydrate. When there is agglomeration alone, precipitation occurs; when hydration is slight and agglomeration predominant, gelatinous precipitate is formed, and when hydration predominates over agglomeration, opaque or opalescent jellies are formed; and when agglomeration is negligible

in comparison with hydration, transparent jellies are formed which maintain their transparency for a long time.

It may be stated that addition of excess of coagulating electrolytes to jelly forming sols always helps agglomeration, and this is why even the transparent jellies formed by excessive addition of electrolytes synerise very rapidly.

It has been shown by Freundlich and Seifriz (*Z. physikal. Chem.*, 1924, **108**, 153) that those sols which display deviations from Poiseuille's law exhibit marked elasticity, and moreover these sols consist of non-spherical particles. It appears that for the formation of a net-work or mesh which has been ascribed to be so necessary for holding water or any other medium, non-spherical particles are essential because these offer the maximum surface for adsorption or hydration.

Increase of temperature also helps the growth of particles and perhaps the tendency of hydration is also accelerated to some extent, and for this reason, jelly is more readily formed at higher temperatures. A sol of tin molybdate containing 91·04 gm. of SnO_2/litre obtained by dialysing a solution of stannic chloride and potassiam molybdate for 24 hours, sets to jelly at various temperatures in different times when half diluted.

TABLE XXVIII.

Temp.	...	90°	70°	60°	50°	40°	24°
Time of setting (min.)	...	1	2	4	7	20	6 hrs.

On warming the clear jelly-forming-sol in a water-bath at a higher temperatare, say 80°, the sol develops turbidity, and finally an opaque or translucent jelly is obtained. It can be seen with naked eyes even that turbidity begins at first near the surface, and before setting of the jelly, it is not spread *uniformly* throughout the solution. In spite of this, a jelly is formed, which is in contradiction to the views held by Weiser (*J. Phys. Chem.*, 1923, **27**, 685; 1922, **26**, 429) that for gelation uniform precipitation throughout the solution is necessary. Weiser has also laid much emphasis on rapid and uniform mixing of the jelly-forming constituents. This factor does not appear to be of much importance, and perhaps is only applicable to pseudo-jellies in which hydration tendency is not so marked and perhaps the setting is due to a

sort of release of supersaturation, as in the case of copper hydroxide prepared from copper acetate and ammonia.

The phenomenon of syneresis is also an important property of some jellies and is best exhibited in the case of zirconium hydroxide, ceric hydroxide, vanadium pentoxide and in the clotting of blood. The jelly of ferric borate or phosphate also undergoes marked syneresis if the coagulating electrolyte is in excess. In reality, syneresis is due to the shrinkage of the hydrated mass. Addition of excess of electrolyte in coagulating the sol gradually accelerates agglomeration and diminishes the hydration and thus shortly after setting the jelly, the excess of electrolyte brings about the syneresis. But the phenomenon of syneresis is not a general rule with all jellies. As has already been said, excessive coagulating electrolytes cause syneresis, and if still more coagulating electrolyte be used, jelly will not set at all and the whole will be precipitated. Thus there are four limits within which the function of electrolyte is restricted:

(*i*) Up to a certain limit—no jelly formation.

(*ii*) Up to the second limit—stable jellies undergoing no marked syneresis.

(*iii*) Between second and third limits—Firm jellies readily synerising.

(*iv*) Above the third limit—no jelly formation, simply precipitation.

Summary.

1. The changes in viscosity with time during the process of gelation have been determined in the case of various jellies. When logarithms of viscosities are plotted against time, straight lines are obtained for a sufficient length of time in the case of chromium hydroxide, stannic hydroxide, mercuric oxide, mercuri-sulpho-salicylic acid, ferric arsenate, ferric phosphate, chromium arsenate, stannic tungstate, stannic molybdate, ferric borate, thorium molybdate, and thorium arsenate jellies. It shows that the gelation is a continuous process. The viscosity-changes are complex in gelation of ferric hydroxide and aluminium hydroxide.

2. In most cases, three stages have been observed during gelation, the first stage corresponding to very little change in viscosity, the second stage where viscosity changes exponentially with time, and the third stage where changes are abrupt.

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3. During the process of gelation, diminution of hydrogen ion concentrations averaging to 50 ± 20 per cent. of the original has been observed.

4. Jellies have been classified according to transparency and explained on the basis of hydration and agglomeration of the particles.

5. A mechanism of the phenomenon of syneresis has also been suggested.

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The Dielectric Constant of Binary Mixtures. Part I. Halides of Methylene and Ethylidene in Benzene.

By P. C. Mahanti and R. N. Das-Gupta.

In a recent paper (*J. Indian Chem. Soc.*, 1928, **5**, 673) it has been shown from the measurement of the temperature-sensitivity of *D.E.K.* by the heterodyne null-method that the dipole moment of methylene bromide is greater than that of methylene chloride and a still greater dipole moment in the case of methylene iodide has been predicted on the basis of the molecular model tentatively suggested therein, treating the electric moment (dipole moment) as a vector quantity. The measurement in the case of methylene iodide could not be taken up by the aforesaid method owing to some technical difficulties such as dissociation at high temperatures and the low vapour pressure of the compound. Hence another method, *i.e.*, the modified Nernst bridge method has been developed to measure the dipole moment of methylene iodide. It is also interesting to undertake the measurements in the case of ethylidene halides to see whether the dipole moments of these compounds follow the same law as that of the methylene halides. It might be pointed out in this connection that in the notice of the *Proc. Roy. Soc.* meeting held on the 21st February, 1929, Hartshorn and Oliver has also adopted the capacity method for the accurate determination of *D.E.K.* of liquids in which they claim an accuracy of 1 in 10,000 approaching therefore results obtained by the heterodyne null-method.

The idea of molecular polarisation as introduced by Debye ("Handbuch der Radiologie," 1925, **6**, 625) has made it possible to calculate the dipole moment of the molecules of a substance from their dielectric constant and density measurements provided they are dissolved in a solvent which has no dipole moment. Non-polar liquids such as carbon tetrachloride, carbon bisulphide, pentane, hexane and benzene are suitable solvents of this type. Thus if a binary mixture consists of a polar liquid (1) obeying Debye law and a non-polar liquid (2) obeying Clausius-Mosotti law, then at a definite temperature the general additive law of polarisation should be satisfied

for different concentrations if the molecules of the two liquids do not react upon one another. Hence the molecular polarisation of such a binary mixture is given by

$$P_{12}=\frac{\epsilon-1}{\epsilon+2}\cdot\frac{M_1C_1+M_2C_2}{d_{12}} \quad \ldots (1)$$

$$=P_1C_1+P_2C_2 \quad \ldots (2)$$

$$\therefore P_1=\frac{P_{12}-P_2C_2}{C_1} \quad \ldots (3)$$

where ϵ = dielectric constant of the mixture having density d_{12} at the room temperature.

M_1, M_2 = molecular weights of the solute and solvent respectively.

C_1, C_2 = molecular fractions ,, ,, ,,

P_1, P_2 = molecular polarisation ,, ,, ,,

But according to Debye, for a polar molecule, $P_1=P_1''+P_1'$ (where P_1'' known as the optical part is due to distortion and P_1' is due to orientation).

$$\therefore P_1=\frac{4\pi N}{3}\nu_1+\frac{4\pi N}{3}\cdot\frac{\mu^2}{3KT}$$

$$=\frac{\epsilon_1-1}{\epsilon_1+2}\cdot\frac{M}{d_1}+20{\cdot}71\times10^{36}\mu^2$$

$$=\frac{n_1^2-1}{n_1^2+2}\cdot\frac{M}{d_1}+20{\cdot}71\times10^{36}\mu^2 \quad \ldots (4)$$

where N = Avogadro number ($6{\cdot}06\times10^{23}$);

ν_1 = Molecular polarisability;

μ = Dipole moment;

K = Boltzmann constant ($1{\cdot}37\times10^{-16}$);

T = Absolute temperature (298°);

ϵ_1, n_1, d_1 = Dielectric constant, refractive index and density respectively of the polar liquid at the room temperature.

Hence combining equations (3) and (4), the dipole moment, μ, of the solute molecule can be calculated.

Experimental.

In the modified Nernst bridge method the necessary condition of silence in the telephone, which is used as a detector, is secured when the leads from the telephone are connected to points which should not only be at the same potential but where the poten tial, *i.e*, the alternating *E.M.F.* should be at the same phase. Since the phase angle depends on the resistance, inductance and capacitance in the arms, a balance of resistance and inductance is therefore required along with a balance of capacitance . This is obtained by the simultaneous adjustment of capacitance and resistance in the proper arm of the bridge. Hence determination of the capacitance is made as if the resistances were not there.

The frequency of the alternating *E. M. F.* was 1000. The Magnanini solution was used for the var iable resistance for a sharp detection of the null-point. The apparat us was well earthed.

The experimental condenser was of parallel plate type. It was first carefully calibrated by using benzene, ethyl ether and octane. The capacity (C_0) was thus found to be $36{\cdot}32\mu\mu F$. The variable standard condenser used was the same as described in a previous paper (*loc. cit.*).

The chemicals used in this investigation were brought from Kahlbaum. The density of each solution was measured with a delicate chemical balance an d a pyknometer. The refractive index of the polar liquids was measured by means of Abbe refractometer.

The experimental condenser was connected in parallel to the arm of the bridge containing the standard variable condenser. The change of capacity (dc) of the experimental condenser due to the introduction of the solution is determined from the readings on the standard condenser. Thus the *D.E.K.* of the solution is calculated from the relation,

$$\epsilon - 1 = \frac{dc}{C_0} = \frac{dc}{36{\cdot}32} \qquad \ldots \quad (5)$$

Results.

For each solution, C_1 and C_2 were calculated from the following relation:

If m_1 gm. of the polar liquid is dissolved in m_2 gm. of non-polar liquid, then

$$Z_1 = \frac{m_1}{M_1} \text{ and } Z_2 = \frac{m_2}{M_2},$$

$$\therefore C_1 = \frac{Z_1}{Z_1 + Z_2} \text{ and } C_2 = \frac{Z_2}{Z_1 + Z_2}.$$

Knowing the value of ϵ from equation (5) P_{12} was calculated for each solution by equation (1).

For each mixture a graph was drawn showing the relation between C_1 and P_{12}. Then from the graph, $P_1 C_1$ was obtained by equation (2) and the values of P_1 at different concentrations were obtained by equation (3). Finally the values of P_1 were plotted against C_1 and the value of P_1 when C_1 is infinitesimal was thus obtained. Then by means of equation (4) the value of μ was evaluated.

TABLE I.

Substance	C_1	d_{12}	C_2	P_{12}
	0·00	0·872	2·26	26·50
	6·21	0·889	2·50	29·41
Methylene	15·62	0·936	2·95	33·30
chloride.	22·77	0·948	3·22	35·90
	29·73	0·968	3·49	37·53
	41·03	1·011	4·61	43·62
	0·00	0·872	2·26	26·50
	4·02	0·923	2·50	29·51
Methylene	7·50	0·961	2·63	31·20
bromide.	10·47	1·000	2·86	33·48
	13·98	1·046	3·05	35·50
	16·70	1·082	3·10	35·79
	19·50	1·121	3·21	39·05

Substance.	C_1.	d_{12}.	C_2.	P_{12}.
	0·00	0·872	2·26	26·50
	2·97	0·933	2·47	29·50
Methylene	9·62	1·084	3·09	36·52
iodide.	12·71	1·153	3·40	39·38
	14·75	1·192	3·55	40·87
	0·00	0·872	2·26	26·50
	5·27	0·892	2·56	30·38
	9·50	0·902	2·81	33·46
Ethylidene	12·40	0·914	3·13	36·62
chloride.	15·01	0·921	3·18	37·06
	21·30	0·938	3·67	41·40
	29·16	0·951	4·12	45·11
	34·34	0·968	4·95	49·00
	0·00	0·872	2·26	26·50
	1·34	0·888	2·35	27·77
Ethylidene	3·40	0·915	2·53	30·18
bromide.	6·67	0·956	2·73	32·75
	0·03	0·985	2·95	35·14
	8·26	1·032	3·28	39·21
	0·00	0·872	2·26	26·50
	0·81	0·891	2·39	27·50
Ethylidene	1·70	0·941	2·58	29·90
iodide.	4·30	0·993	2·78	32·25
	6·70	1·045	2·95	34·56
	7·50	1·062	3·11	36·54

TABLE II.

Chemical formula.	n_1.	d_1.	P_1.	P_1''.	P_1'.	$\mu \times 10^{18}$.
CH_2Cl_2	1·425	1·378	70·0	15·78	54·22	1·61
CH_2Br_2	2·498	1·525	95·5	21·05	74·45	1·89
CH_2I_2	3·285	1·618	122·2	28·56	93·64	2·12
CH_3CHCl_2	1·417	1·180	100·0	21·08	78·92	1·95
CH_3CHBr_2	1·512	2·033	120·9	27·62	93·28	2·12
CH_3CHI_2	1·609	2·775	144·0	35·15	108·85	2·30

Discussion.

Williams (*J. Amer. Chem. Soc.*, 1927, **49**, 1676) and others have noticed that benzene, though ordinarily considered to be non-polar, has an electric moment $0{\cdot}06 \times 10^{-18}$ *C.G.S.* electrostatic units. Hence our results are correct up to $0{\cdot}06 \times 10^{-18}$.

The measurements on CH_2Cl_2 and CH_2Br_2 have also been repeated by this method to ensure correctness of the calibration and adjustment of the instrument. They agree remarkably well with the values obtained by the heterodyne method, thus:

	Mahanti and Sen-Gupta (*loc. cit.*).	Sanger (*Physikal. Z.*, 1926, **28**, 556).
CH_2Cl_2	$1{\cdot}62 \times 10^{-18}$	$1{\cdot}59 \times 10^{-18}$
CH_2Br_2	$1{\cdot}91 \times 10^{-18}$	

The results presented in this paper further support the mechanism of the molecular model which was tentatively suggested in the previous paper (*loc. cit.*), *viz.*, that the CH_2Cl_2 molecule may be regarded as a distorted tetrahedron with the Cl-atoms at its two corners due to the interaction of the electronic orbits, the orbits of Cl-atoms as well as that of CH_2^{++} will be distorted. These distortions will develop moments in the two Cl-atoms as in the CH_2^{++}. The direction of the moment in the two Cl-atoms will be mutually inclined to each other and the moment of CH_2^{++} will be making equal angles with the direction of the moments in each Cl-atom. Treating now the electric moment as a vector quantity we can resolve the moments of the Cl-atoms and the net dipole moment of the molecule is the resultant of the moment of the CH_2^{++} and the resolved part of the moments of the atoms operating in the opposite direction. When Br is substituted for Cl, owing to larger nuclear change of Br, they are mutually separated from each other to a large extent than in the case of Cl-atoms. This results in producing a net dipole moment larger than that of CH_2Cl_2. Similarly the still larger value for CH_2I_2 can be explained. The values obtained in the case of ethylidene halides can be interpreted in a similar way. This view seems to have been supported recently by William (*J. Amer. Chem. Soc.*, 1928, **50**, 2350), and it may be also pointed out that in the first number of the new series of the *Annalen der Physik*,

Brüche has reviewed all the results obtained up to the present in getting an idea of the shape of the methane molecule and he suggested from his slow electron bombardment method that the structure of methane is perfectly symmetrical resembling an inert gas constitution similar to krypton and the addition of halogen ions produces the distortion of the structure as conceived in this paper.

Our best thanks are due to Prof. P. N. Ghosh for his kind interest and encouragement during the course of the work.

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Kinetic Salt Effect. Part III. Influence of Non-electrolytes on Salt Effect in Ionic Reactions.

By A. N. Kappanna.

It was shown in a previous communication from this laboratory that the variation of the kinetic activity factor with total ionic strength in the reaction between monobromacetate and thiosulphate ions is in good agreement with the variation rate calculated on the basis of Debye-Hückel limitation equation for the activity coefficient of an ion in dilute solutions up to a total ionic strength of $0{\cdot}014\mu$ (*J. Indian Chem. Soc.*, 1929, **6**, 45). This simple method of testing theory by velocity measurements can advantageously be extended to non-aqueous sclutions or solutions in mixed solvents.

In the equation deduced from Brönsted's (or Soper's) theory, for aqueous solutions in the neighbourhood of 25°,

$$\log K = Constant \pm Z_A Z_B \sqrt{\mu} \qquad \ldots \quad (1)$$

we see that the velocity constant would be affected if to the reaction mixture we were to add an electrolyte, be it one of the reacting components or a neutral salt. On the other hand, the addition of a non-electrolyte should have no effect. It should be remembered at the same time that the above equation has been deduced on the basis of Debye's equation for the activity coefficient of an ion,

$$-\log f_i = \frac{\epsilon^2 - z^2}{2DkT} \sqrt{\frac{4\pi.\epsilon^2}{DkT} \Sigma n_i^2 . z_i^2} \qquad \ldots \quad (2)$$

which shows that the dielectric constant of the ionising medium has a profound influence on the activity coefficient of an ion and consequently on the variation of the kinetic activity factor. It is well-known that non-electrolytes like alcohol and cane sugar lower the dielectric constant of water to a considerable extent. From the standpoint of equation (1) all that can be said therefore is that so

long as the amount of non-electrolyte added to an aqueous solution is not too great to bring about a change in the nature of the solvent, its influence on the activity coefficient of any one of the ions or the kinetic activity factor may be negligible. But, when the amount of non-electrolyte added is large enough, the lowering in the dielectric constant becomes marked and from theory we should expect a marked difference in the variation of the kinetic activity factor, whatever the effect of the non-electrolyte on the velocity constant at a particular total ionic concentration may be.

While the need for more data in pure aqueous solutions concerning ions of different characteristics remains, it can be said that so far as aqueous solutions are concerned, the investigations of Brönsted and La Mer and others (*J. Amer. Chem. Soc.*, 1924, **46**, 555) have provided ample material in proof of Debye-Hückel theory. The same, however, cannot be said of solvents other than water or solvent mixtures having water as one of the components. Attempts have been made by Scatchard (*J. Amer. Chem. Soc.*, 1925, **47**, 2098 ; Noyes and Baxter (*ibid*, 1925, **47**, 2122) and Nonhebel and Hartley (*Phil. Mag.*, 1925, **50**, 2122) among others to test the validity of Debye's theory in mixtures of alcohol and water and pure alcohols. They considered the data for hydrochloric acid in these different solvents and found that even in the case of this simple uni-univalent electrolyte, the agreement between theory and experimental results was not close. More recently Brönsted and Williams (*J. Amer. Chem. Soc.*, 1928, **50**, 1338) have found from solubility measurements that in aqueous-alcoholic and sugar solutions, the agreement between theory and experiment, though not quantitative, is yet not unsatisfactory. In view of the paucity of data on the effect of non-electrolytes on the activity coefficients of ions of different valence types in aqueous solutions, velocity measurements of ionic reactions in solvent mixtures would afford valuable evidence either for or against equation (2).

The present investigation was undertaken with the object of studying the kinetics of the reaction between monobromacetate and thiosulphate ions, from the above standpoint, in mixtures of alcohol and water and cane sugar and water, as the dielectric constants of these mixtures are fairly well known. This reaction, a detailed investigation of which was reported in Part II (*loc. cit.*) is quite suitable for our purpose as both the reacting components are quite neutral towards the non-electrolytes, alcohol and sugar.

Experimental.

The way in which the reaction was followed was the same as in Part II, the usual precautions for the purification of the materials necessary being observed.

Aqueous—Alcoholic Solutions.—Measurements have been made with pure water, 20% 40%, 60% and 80% alcoholic solutions (the figures refer to volume per cent.). Tables I-IX give data obtained with 80% alcoholic solutions at 25°. The symbols T and Br are employed in the following tables for thiosulphate and bromacetate respectively.

Table I.

$CH_2Br.COONa = 0{\cdot}02M$; $Na_2S_2O_3 = 0{\cdot}01M$.

Ionic strength $= 0{\cdot}05\mu$; 10 c.c. titrated.

Time in minutes.	T.	Br.	K.
0	8·45 c.c.	18·45 c.c.	—
10	7·25	17·25	0·8579
20	6·30	16·30	0·8487
30	5·50	15·50	0·8510
40	4·80	14·80	0·8625
50	4·25	14·25	0·8556
70	3·35	13·35	0·8579
		Mean	0·8556

Table II.

$CH_2Br.COONa = 0{\cdot}005M$; $Na_2S_2O_3 = 0{\cdot}01M$.

Ionic strength $= 0{\cdot}035\mu$; 10 c.c. titrated.

Time in minutes.	T.	Br.	K.
0	9·55 c.c.	4·55 c.c.	—
30	8·75	3·75	0·7052
60	8·15	3·15	0·6969
90	7·65	2·65	0·7079
150	6·95	1·95	0·7038
210	6·50	1·50	0·6900
360	5·80	0·80	0·6900
		Mean	0·6989

TABLE III.

$CH_2Br.COONa = 0{\cdot}008M$; $Na_2S_2O_3 = 0{\cdot}004M$.

Ionic strength $= 0{\cdot}02\mu$; 25 c.c. titrated.

Time in minutes.	T.	Br.	K
0	9·80 c.c.	19·80 c.c.	—
30	8·55	18·55	0·5922
60	7·50	17·50	0·5980
90	6·35	16·65	0·5945
120	5·95	15·95	0·5750
200	4·50	14·50	0·5825
380	2·50	12·50	0·5951
		Mean	0·5981

TABLE IV.

$CH_2Br.COONa = 0{\cdot}002M$; $Na_2S_2O_3 = 0{\cdot}004M$;

Ionic strength $= 0{\cdot}014\mu$; 25 c.c. titrated.

Time in min.	T.	Br.	K.
0	9·90 c.c.	4·90 c.c.	—
60	9·40	4·40	0·4638
150	8·75	3·75	0·4798
250	8·20	3·20	0·4726
420	7·50	2·50	0·4680
600	6·95	1·95	0·4726
		Mean	0·4713

TABLE V.

$CH_2Br.COONa = 0{\cdot}004M$; $Na_2S_2O_3 = 0{\cdot}002M$;

Ionic strength $= 0{\cdot}01\mu$; 50 c.c. titrated.

Time in min.	T.	Br.	K.
0	9·90 c.c.	19·90 c.c.	—
60	8·95	18·95	0·4312
120	8·15	18·15	0·4266
180	7·40	17·40	0·4347
300	6·25	16·25	0·4289
520	4·65	14·65	0·4312
750	3·50	13·50	0·4355
		Mean	0·4310

TABLE VI.

$CH_2Br.COONa = 0{\cdot}001M$; $Na_2S_2O_3 = 0{\cdot}0025M$.

Ionic strength $= 0{\cdot}0085\mu$; 100 c.c. titrated.

Time in min.	T.	Br.	K.
0	24·90 c.c.	9·90 c.c.	—
100	24·00	9·00	0·3910
200	23·15	8·15	0·4039
300	22·45	7·45	0·4010
450	21·55	6·55	0·3986
600	20·75	5·75	0·4002
750	20·10	5·10	0·3986
		Mean	0·3990

TABLE VII.

$CH_2Br.COONa = 0{\cdot}001M$; $Na_2S_2O_3 = 0{\cdot}002M$;

Ionic strength $= 0{\cdot}007\mu$; 50 c.c. titrated.

0	9·90 c.c.	4·90 c.c.	—
120	9·50	4·50	0·3660
180	9·325	4·325	0·3657
300	9·00	4·000	0·3591
420	8·70	3·70	0·3634
600	8·30	3·30	0·3648
1440	7·10	2·10	0·3585
		Mean	0·3626

TABLE VIII.

$CH_2Br.COONa = 0{\cdot}002M$; $Na_2S_2O_3 = 0{\cdot}001M$;

Ionic strength $= 0{\cdot}305\mu$; 50 c.c. titrated.

0	4·95 c.c.	9·95 c.c.	0·3045
240	4·30	9·30	0·3089
480	3·80	8·80	0·3089
750	3·30	8·30	0·2990
1550	2·30	7·30	0·3044
2160	1·75	6·75	0·3013
		Mean	0·3036

TABLE IX.

$CH_2Br.COONa = 0{\cdot}001M$; $Na_2S_2O_3 = 0{\cdot}0005M$;
Ionic strength $= 0{\cdot}0025\mu$; 100 c.c. titrated.

Time in min.	T.	Br.	K.
0	4·875 c.c.	9·875 c.c.	—
250	4·60	9·60	0·2337
480	4·375	9·375	0·2309
780	4·10	9·10	0·2323
1500	3·55	8·55	0·2300
2160	3·10	8·10	0·2346
		Mean	0·2323

Table X contains a summary of data obtained with the different alcoholic solutions. The data with pure aqueous solutions are also included for purposes of comparison.

TABLE X.

Velocity Constants.

μ	Water.	20%.	40%.	60%.	80%.
0·0025	0·2970	0·2576	0·2093	0·2136	0·2328
0·005	0·3306	0·3059	0·2599	0·2716	0·3036
0·007	0·3511	0·3427	0·3082	0·3176	0·3626
0·0085	0·3615	0·3680	0·3289	0·3528	0·3990
0·010	0·3727	0·3841	0·3473	0·3841	0·4310
0·014	0·3029	0·4117	0·3841	0·4299	0·4713
0·020	0·4288	0·4531	0·4554	0·4745	0·5891
0·035	0·4825	0·5124	0·5313	0·5704	0·6989
0·050	0·5244	0·5474	0·5796	0·6532	0·8556
0·070	0·5571	0·5635	0·6357	0·7406	—
0·085	0·5923	0·5835	0·6601	—	—

A glance at the table shows that no general relationship can be drawn between the concentration of alcohol and its effect upon the velocity constant. In a 20% solution of alcohol the velocity at lower concentrations is decidedly lesser than in aqueous solutions up to about $0{\cdot}010\mu$ and beyond this concentration the velocity is slightly higher than in aqueous solutions. In a 40% solution of alcohol up to $0{\cdot}014\mu$ the velocity constants have values

lower still than in 20% alcoholic solutions and then the values rise much higher. In 60% alcoholic solutions, below $0{\cdot}01\mu$ the velocity constants are lower than in aqueous solutions and then they rise higher whereas throughout the range examined the values are always higher than in 40% solution. In 80% solution the constants are always very much higher than in 60% solution. The velocity constants except for $0{\cdot}0025\mu$ and $0{\cdot}005\mu$, are even very much higher throughout than in water. It thus becomes clear that it is unsafe to conclude from a series of measurements at any particular ionic strength with solvent mixtures of different compositions, anything with regard to the relationship between the concentration of the non-electrolyte and the velocity of the reaction. Senter (*J. Chem. Soc.*, 1915, **107**, 1071) found in his study of the reaction between sodium monobromacetate and sodium methoxide in aqueous-alcoholic solutions that the reaction proceeded with the maximum velocity in a 60% alcoholic solution (Senter's results were confined only to one total ionic concentration.) The first, second, third and fourth horizontal columns in Table X show that the velocity constant passes through a minimum in a 40% alcoholic solution. The same can be said to be the case with the 5th and 6th columns, if we exclude the data for water. The remaining columns do not show any maximum or minimum points. In these cases the velocity progressively increases with the increase in alcohol content of the solvent.

Debye-Hückel slopes.—We have seen before that in the case of pure aqueous solutions, $\frac{d \log k}{d\sqrt{\mu}}$ found is almost exactly equal to the calculated Debye-Hückel slope. Fig. 1 gives the curves in which $\log K$ is plotted against $\sqrt{\mu}$ for dilute solutions in aqueous alcohol—water mixtures. Table XI gives the calculated and experimentally determined slopes.

TABLE XI.

Alcohol.	Slope (found).	Slope (calc.).	Difference.
20%	3·75	2·50	50%
40%	4·66	3·21	48·2%
60%	5·10	4·45	14·60%
80%	5·75	6·65	13·50%

For the calculations involved, the values for the dielectric constants of the alcoholic mixtures have been taken from the paper of

Fürth (*Ann. Physik*, 1923, **70**, 63). The values of Fürth coincide almost with the results of Nernst (*Z. physikal. Chem.*, 1890, **14**, 660). It will be seen that in 20, 40 and 60 per cent. alcoholic mixtures of water the slopes found are very much higher than the calculated slopes, while in 80% solution the reverse is the case. In 20 and 40 per cent. solutions the divergence from theory is very great while in 60 and 80 per cent. solutions it is not very great. However, even in the last two cases, the agreement with theory cannot be said to be even a rough one. Brönsted and Williams (*loc. cit.*) found from solubility measurements that the Debye-Hückel slopes calculated from theory differed from experimental ones by about 10-15%. Yet assuming that there was some uncertainty about the values of the dielectric constants of the mixtures, they concluded that their results are in agreement with the Debye-Hückel theory. It appears to the author, however, that it is a little too much to assume that the dielectric constant measurements are so much in error. So far as the velocity measurements of the present investigation indicate, Debye-Hückel theory does not quantitatively predict the course of the reaction, although the slopes are in the direction indicated by the theory. Table XII gives the velocity constants at different ionic concentrations in the different alcoholic solvents at 35°.

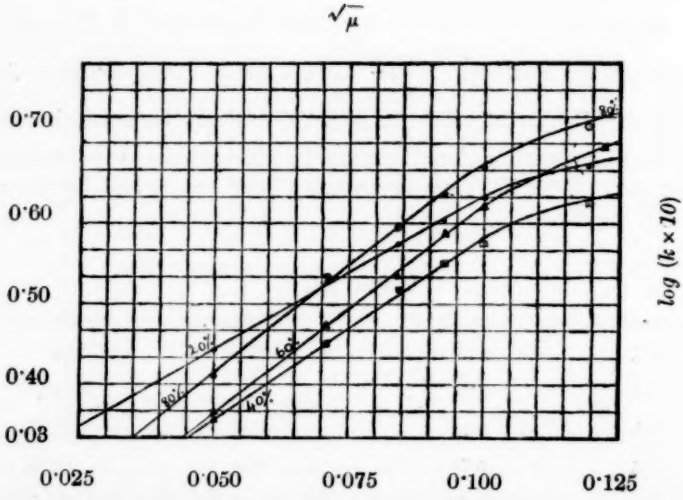

Fig. 1.

TABLE XII.

Velocity Constants.

μ.	20%.	40%.	60%.	80%.
0·0025	0·5428	0·4255	0·5018	0·5405
0·0050	0·6440	0·5267	0·6410	0·7047
0·007	0·7199	0·6187	0·7463	0·8418
0 0085	0·7820	0·6624	0·8255	0·9287
0·010	0·8073	0·7015	0·9050	1·0005
0·014	0·8625	0·7682	1·0106	1·2010
0·020	0·9522	0·9200	1·1178	1·3800
0·035	0·0787	1·0695	1·3404	1·6054
0·050	1·1500	1·1730	1·5295	1·9842
0·070	1·1833	1·2765	1·7273	—
0·085	1·2254	1·3363	—	—

Table XIII gives the temperature coefficients $K_{35°}/K_{25°}$ in these different cases.

TABLE XIII.

$K_{35°}/K_{25°}$.

μ.	20%.	40%.	60%.	80%.
0·0025	2·107	2·033	2·347	2·320
0·0050	2·105	2·024	2·360	2·321
0·0070	2·100	2·007	2·349	2·321
0·0085	2·127	2·014	2·311	2·327
0·0100	2·091	2·019	2·356	2·321
0·0140	2·095	2·000	2·350	2·550
0·0200	2·102	2·020	2·355	2·342
0·0350	2·105	2·013	2·349	2·297
0·0500	2·108	2·024	2·340	2·319
0·0700	2·100	2·008	2·322	—
0·0850	2·098	2·024	—	—
Mean	2·103	2·017	2·344	2·321

It is to be observed that as in the case of aqueous solutions, in these cases also the temperature coefficient over the entire range of ionic concentrations remains absolutely steady. But each alcoholic solution has its own temperature coefficient. This is of course to be expected but it is rather queer that there is no regularity about the variation of the temperature coefficient with the percentage of alcohol.

Cane Sugar Solutions.

Fürth has also determined the dielectric constants of solutions of cane sugar in water. It is possible to prepare cane sugar solutions having the same dielectric constants as certain alcoholic solutions and it was thought that velocity measurements in these sugar mixtures might throw some light on the point whether the velocity at any ionic concentration is determined by factors other than dielectric constant. From this standpoint cane sugar solutions serve a very useful purpose as they happen to be very viscous as compared with water-alcohol mixtures. Table XIV gives the data at 25° with 30% and 50% (by weight) sugar solutions.

TABLE XIV.

Velocity Constants.

μ.	30% sugar.	50% sugar.
0·0025	0·2820	0·2690
0·005	0·3320	0·3372
0·007	0·3491	0·3681
0·010	0·3832	0·4159
0·014	0·4180	0·4395
0·020	0·4613	0·4820
0·035	0·5290	0·5701

Here also, as in the case of alcoholic solutions, we find that initially, *i.e.*, at low concentrations, the velocity constants are lower than in the case of pure water but soon they begin to rise and go above the values in water as the ionic concentration rises. The

rate of rise in 50% sugar solutions is very much higher than in 30% solutions. The 30% and 50% sugar solutions have dielectric constants 67 and 49 respectively. For these mixtures the calculated Debye-Hückel slopes in the ideal region are 2·568 and 4·104 respectively. Curves obtained by plotting the data in Table XIV give for $\frac{d \log k}{d\sqrt{\mu}}$ the values 2·6 and 3·6 for 30% and 50% sugar solutions respectively. In the first case the agreement with theory is excellent while in the latter case the divergence is not much as compared with the divergences observed in the case of alcoholic solutions. It can therefore be said that so far as the ions in our reaction are concerned, up to a limit of about $0{\cdot}015\mu$ and $0{\cdot}010\mu$ in the cases of 30% and 50% sugar solutions respectively (deduced from graphs), the Debye-Hückel expression fairly quantitatively predicts the courses of the reaction.

It is to be observed at the same time that viscosity does not seem to have any marked effect on the velocity of reaction.

Summary.

(1) A study of the kinetics of the reaction between monobromacetate and thiosulphate ions has been made at various ionic concentrations beginning from $0{\cdot}0025\mu$ in 20%, 40%, 60% and 80% solutions of alcohol in water and in 30% and 50% solutions of sugar in water.

(2) The temperature coefficients of the rates of reaction at the different ionic concentrations and in the different alcoholic solvents have been measured. The temperature coefficient remains absolutely steady in the same solvent over the entire range of ionic concentrations. The reaction velocity has a definite temperature coefficient in each of the solvents, but there is no regularity in the variation of the temperature coefficient with the percentage of alcohol.

(3) The slopes $\left(\frac{d \log k}{d\sqrt{\mu}}\right)$ found in the case 20 and 40 per cent. mixtures of alcohol in water are nearly 50% greater than the slopes calculated on the basis of Debye-Hückel limitation equation, while the slope in 60% alcohol is 15% higher and in 80% alcohol it is 14% lesser than the calculated slopes.

(4) No general relationship could be traced between the percentage of alcohol and the velocity constant although some regularity may be found at any particular ionic concentration.

(5) The results obtained with sugar solutions show greater agreement with Debye-Hückel theory. The values of $\left(\frac{d \log k}{d\sqrt{\mu}}\right)$ found in the case of 30% and 50% sugar solutions are 2·6 and 3·6 respectively while the calculated values are 2·568 and 4·104 respectively. The viscosity of sugar solutions does not seem to affect the velocity of reaction to any appreciable extent.

I have enjoyed the privilege of discussing the several problems connected with the velocity of ionic reactions with my professor, Dr. J. C. Ghosh. I take this opportunity of expressing my gratitude to him for the kind interest he has taken in my work.

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Influence of Light on Some Colloids.

By Miss Sheila Roy.

In publications (*Kolloid Z.*, 1922, **31**, 16 ; *J. Phys. Chem.*, 1929, **33**) from these laboratories the influence of light on some properties of colloids has been investigated. We have observed that sols can be divided into two classes. In one class the stability of the sol towards electrolytes increases and in the other the stability decreases on exposure to light. With some sols the electric conductivity increases whilst with others it decreases on exposure to light. Measurements of the absorption spectra of the exposed and unexposed sols showed more marked absorption of light in the cases of ferric hydroxide, arsenious sulphide and Prussian blue and less absorption in the cases of gum dammar, mastic, etc. We have also shown that sols of manganese dioxide, ceric hydroxide, copper ferrocyanide and Odèn sulphur coagulate completely on exposure to sunlight.

In this communication we have investigated the influence of sunlight and light from a thousand watt gas-filled tungsten filament lamp on the (*a*) coagulation, (*b*) electric conductivity, and (*c*) extinction coefficient of sols of stannic hydroxide, aluminium hydroxide, thorium hydroxide, antimony sulphide, mercuric sulphide, arsenious sulphide, cupric ferrocyanide and uranium ferrocyanide.

The sols were exposed to light in small stoppered Jena glass bottles or silica vessels. The extinction coefficients were determined by a Nutting's spectrophotometer.

Experimental.

Stannic hydroxide.

The stannic hydroxide was prepared at the ordinary temperature by adding ammonium hydroxide to stannic chloride. The stannic hydroxide thus obtained was washed two or three times to free it from electrolytes partially. On further addition of water it turned immediately to a sol, which was dialysed for 10 days.

TABLE I.

Concentration = 6·66 gms. of SnO_2 per litre. Volume of mixture = 10 c.c. Amount of sol taken = 1 c.c. Time allowed for coagulation = 1 hour.

Electrolyte used.	Amount needed for coagulation. Unexposed.	Exposed.	
N/2·5-KCl	0·80 c.c.	0·55	The sol was exposed for 169 hrs. 15 mins. to sunlight.
N/500-$BaCl_2$	2·50	2·00	

Electric conductivity at 25°.

Sp. conductivity for unexposed sol ... ... 0·005794 mhos.

Sp. conductivity for sol exposed to sunlight for 237 hrs. 0·006164 ,,

Extinction coefficients.

Sol.	Extinction coefficient.
Unexposed Sb_2S_3	0·0
Sb_2S_3 exposed to sunlight for 201 hrs. and 40 mins. ...	0·1

Aluminium hydroxide.

Aluminium hydroxide was precipitated by ammonium hydroxide on aluminium nitrate solution at the ordinary temperature. The precipitate was completely freed from electrolytes by repeated washings and was peptised to a turbid sol by the addition of a few drops of dilute hydrochloric acid.

TABLE II.

Concentration = 15·42 gms. of Al_2O_3 per litre. Total volume taken = 10 c.c. Amount of sol taken = 0·5 c.c. Time allowed for coagulation = 1 hour.

Electrolyte used.	Amount of electrolyte required for coagulation. Unexposed sol.	Sol exposed for 85 hrs. to sunlight.
N-KCl	3·25 c.c.	3·0 c.c.
N/500-K_2SO_4	4·10	4·0

Electric conductivity at 25°.

Sp. conductivity for sol kept in the dark. ... ... 0·001821 mhos.

Sp. conductivity for sol. exposed to sunlight for 133 hrs. and 25 mins. ... ... 0·001888 ,

Extinction coefficient.

Sol.	Extinction coefficient.
Unexposed $Al(OH)_3$	0·8
$Al(OH)_3$ exposed for 94 hrs.	0·72

Thorium hydroxide.

A solution of Kahlbaum's pure thorium nitrate was filtered and boiled for about an hour, and the boiled solution was subjected to hot dialysis for 7 days. A clear transparent sol of thorium hydroxide was obtained.

TABLE III.

Concentration = 6·1 gms. of ThO_2 per litre. Volume of mixture = 10 c.c. Amount of sol taken = 0·5 c.c. Time allowed for coagulation = 1 hour.

Electrolyte used.	Amount needed for coagulation.	
	Unexposed sol.	Sol exposed for 58 hrs. 45 mins. to sunlight.
5·33 *N*-KCl	1·85 c.c.	1·25 c.c.
N/50-K_2SO_4	0·60	0·50
N/100-K_3-citrate	1·30	0·60

Electric conductivity at 25°.

Sp. conductivity for sol kept in the dark.	Sp. conductivity for sol exposed for 106 hrs, 10 mins. to sunlight.
0·009581 mohs.	0·01284 mhos.
0·009796	0·01278

Extinction coefficients.

Sol.	Extinction coefficient.
$Th(OH)_4$ sol kept in the dark	0·03
Sol exposed to sunlight for 75 hrs. 30 mins. ...	0·07

Mercuric sulphide.

Mercuric oxide was precipitated by the action of pure potassium hydroxide solution on mercuric chloride solution. The precipitate was freed from alkali and chloride by repeated washing first with cold and then with hot water. The purified mercuric oxide was boiled in a Jena flask with conductivity water. To the saturated solution of mercuric oxide thus obtained a slow current of hydrogen sulphide

was passed and a black sol of mercuric sulphide was obtained. The excess of hydrogen sulphide was removed by passing a current of hydrogen. By this method one can readily obtain a pure sol of mercuric sulphide.

TABLE IV.

Concentration of sol = 0·11 gm. of HgS per litre. Volume of mixture = 5 c.c. Amount of sol taken = 2·5 c.c. Time allowed for coagulation = 1 hour.

Electrolyte used.	Amount needed for coagulation.	
	Unexposed sol.	Sol exposed to sunlight for 88 hrs. 15 mins.
N/10-KCl	1·2 c.c.	0·4 c.c.
N/40-$BaCl_2$	0·3	0·15

Electric conductivity at 25°.

Sp. conductivity for sol kept in the dark	0·0002146 mhos.
Sp. conductivity for sol exposed to sunlight for 147 hrs. 45 mins.	0·0002869.

Extinction coefficients.

Sol.	Extinction coefficient.
HgS kept in the dark ...	1·25
Sol exposed to sunlight for 117 hrs. 5 mins.	1·40

Antimony sulphide.

Hydrogen sulphide was passed through a solution of potassium antimony tartrate. An orange coloured sol of antimony sulphide was obtained which was freed from sulphuretted hydrogen and tartrate by dialysis at the ordinary temperature for 10 days.

TABLE V.

Concentration of sol = 0·53 gm. of Sb_2S_3 per litre. Vol. of mixture = 10 c. c. Amount of sol taken = 1 c.c. Time allowed for coagulation = 1 hour.

Electrolyte used.	Amount needed for coagulation.	
	Unexposd sol.	Sol exposed to sunlight for 27 hrs 20 mins.
N-KCl	0·55 c. c.	0·80 c. c.
N/40-$BaCl_2$	0·80	1·60

Electric conductivity at 25.°

The sol coagulated after 52 hrs. and 50 minutes' exposure in a glass vessel so that the electric conductivity and extinction coefficients could not be noted.

In the following experiments antimony and arsenious sulphide sols were exposed to light in silica vessels.

Antimony sulphide.

The sol was prepared in the usual way but was not subjected to dialysis as it was a clear one.

TABLE VI.

Concentration of the sol = 0·9430 gm. of Sb_2S_3 per litre. Vol. of mixture = 5 c. c. Amount of sol taken = 1 c. c. Time allowed for coagulation = 1 hour.

Electrolyte used.	Amount needed for coagulation.	Nature of sol taken.
N/10-KCl	2·2 c. c.	Kept in the dark.
	2·2	Exposed to light from a 1000-Watt lamp for 3 hos.
	2·5	,, ,, ,, ,, ,, 4½ ,,
	2·5	,, ,, to sunlight for 3 hrs.
	2·4	Exposed to light from a 1000-Watt lamp for 9 ,,
	2·4	Kept in the dark.
	2·5	,, ,, ,,
	2·2	Exposed to sunlight for 13 hrs. 18 mins.

Electric conductivity at 25.°

Sp. conductivity for sol kept in the dark.	Sp. conductivity for sol exposed to light.	Nature of light and time.
0·000527	0·000529	1000-Watt lamp for 3 hrs.
	0·000632	,, ,, ,, 4½ hrs.
	0·000553	,, ,, ,, 9 ,,
	0·000682	Sunlight for 3 hrs.
	0·00149	,, 13 hrs. 18 mins.

Extinction coefficients.

Sol.	Extinction coefficient.
Sb_2S_3 kept in the dark	0·60
Sb_2S_3 exposed to light from a 1,000 Watt lamp for 4½ hrs.	0·49
Sb_2S_3 exposed to light from a 1,000 Watt lamp for 9 hours	0·52

Arsenious sulphide.

The sol was prepared by passing hydrogen sulphide in a concentrated solution of arsenious oxide in water. In order to free it from hydrogen sulphide a current of hydrogen was passed.

TABLE VII.

Concentration of the sol = 52·79 gms. As_2S_3 per litre. Vol. of mixture = 5 c. c. Amount of sol taken = 1 c. c. Time allowed for coagulation = 1 hour.

Electrolyte used.	Amount needed for coagulation.	Nature of sol.
N/10-KCl	3·10 c. c.	Kept in the dark.
	3·20	Exposed to sunlight for ½ hr.
	3·10	,, ,, 1 ,,
	3·05	,, ,, 2 hrs.
	3·00	,, ,, 3 ,,
	2·90	,, ,, 4 hrs. 45 mins.

Electric conductivity.

Sp. conductivity for sol kept in the dark.	Sp, conductivity for sol exposed to sunlight.	Time of exposure.
	0·000364	1 hr.
	0 000439	2 hrs.
0·000303	0·000502	3 ,,

Extinction coefficients.

Sol.	Extinction coefficients.
As_2S_3 kept in the dark ...	1·73
As_2S_3 exposed for ½ hour to sunlight ...	1·48
As_2S_3 exposed for 3 hours to sun light ...	1·83

Uranium ferrocyanide.

Solutions of uranium nitrate and potassium ferrocyanide were mixed at the ordinary temperature and a brownish red sol of uranium ferrocyanide was obtained in presence of an excess of potassium ferrocyanide. The sol was dialysed for 12 days in order to free it from potassium ferrocyanide.

TABLE VIII.

Concentration of sol = 4·0 gms. uranium ferrocyanide per litre. Vol. of the mixture = 5. c. c. Amount of sol taken = 1 c. c. Time allowed for coagulation = 1 hour.

Electrolyte used.	Amount needed for coagulation.	
	Unexposed sol.	Exposed for 10 hrs. 20 mins.
N/2·5-KCl	2·5 c. c.	2·3 c. c.
N/40-$BaCl_2$	1·9	1·7

Electric conductivity at 25.°

Completely coagulated after 33 hrs. 15 mins'. exposure to sunlight. Hence electric conducivity could not be determined.

Extinction coefficients.

Sol.	Extinction coefficient.
Uranium ferrocyanide kept in in dark	3·8
Uranium ferrocyanide exposed to sunlight for 23 hrs. 5 mins ...	2·2

In the following experiments uranium and cupric ferrocyanide sols were exposed to sunlight in silica vessels.

Uranium ferrocyanide.

TABLE IX.

Concentration of the sol = 0·955 gm. uranium ferrocyanide per litre. Vol. of mixture = 5 c. c. Amount of sol taken = 1 c. c. Time allowed for coagulation = 1 hour.

Electrolyte used.	Amount needed for coagulation.	Nature of sol.
N/10-KCl	1·6 c. c.	Kept in the dark.
	1·55	Exposed to sunlight for 2½ hours.
	1·50	,, ,, ,, ,, 5 ,,
	1·40	Kept in the dark.
	1·60	Exposed to sunlight for 1 hour.

The sol coagulated so that the conductivity and extinction coefficient results could not be noted.

Cupric ferrocyanide.

Concentrated solutions of cupric sulphate and potassium ferrocyanide (excess) were mixed together. The mixture was allowed to dialyse for 20 days.

TABLE X.

Concentration of the sol = 22·58 gms. of cupric ferrocyanide per litre. Vol. of the mixtue = 5 c.c. Amount of sol taken = 1 c.c. Time allowed for coagulation = 1 hour.

Eectrolyte used.	Amount needed for coagulation.	Nature of sol.
N/10-KCl	0·65 c. c.	Kept in the dark.
	0·70	Exposed to sunlight for 1 hour.
	0·85	Exposed to sunlight for 2 hours.
	0·75	Exposed to sunlight for 3 ,,
	0·85	Kept in the dark.
	0·80	Exposed to sunlight for 25 hours.

Electric conductivity.

Sp. conductivity for sol kept in dark.	Sp. conductivity for sol exposed to sunlight.	Time of exposure.
	0·000134	1 hour.
	0·000165	2 hrs.
0·000184	0·000168	3 ,,

Extinction coefficients.

Sol.	Extinction coefficient.
Sol kept in the dark	2·98
Sol exposed to sunlight for 2 hrs....	2·48
,, ,, ,, 3 ,, ...	8·08

The experimental results on the influence of light on colloids show that sols of $Sn(OH)_4$, $Th(OH)_4$, $Al(OH)_3$ and HgS become unstable towards electrolytes on exposure to light. The electric conductivity of these sols increases on exposure.

On the other hand, sols of Sb_2S_3, As_2S_3, uranium ferrocyanide and cupric ferrocyanide, when exposed to light for a short time,

become stable, but on longer exposure they become unstable towards electrolytes. On further exposure Sb_2S_3, HgS, and uranium ferrocyanide coagulate completely.

In papers (*Z. anorg. Chem.*, 1927, **162**, 237 ; **168**, 209; *Kolloid Z.* 1927, **42**, 120) published from these laboratories we have shown that sols of ferric hydroxide, aluminium hydroxide, stannic hydroxide, etc., become more conducting, less viscous and less stable towards electrolytes on ageing. Our results show that the effect of light is of the same type as that of ageing on the hydroxide sols. We (*J. Phys. Chem.*, 1925, **29**, 659 ; *Kolloid Z.*, 1926, **38**, 14 ; **39**, 346) have also shown that sols of arsenious sulphide, antimony sulphide and cupric and uranium ferrocyanides are appreciably hydrolysed in aqueous solutions and this hydrolysis makes the sol more stable towards electrolytes. Moreover we have also shown that on ageing the sols become more hydrolysed and more stable towards electrolytes up to a limiting value. The foregoing results show that under the influence of light these sols become more hydrolysed and more stable towards electrolytes when exposed for a short time especially in filica vessels. On longer exposure the sols become unstable towards electrolytes. This behaviour is due to the fact that in the cases of arsenious and antimony sulphides, the stabilising electrolyte hydrogen sulphide is oxidised by air. Moreover, several of the sulphides are oxidised also to sulphur and thionic compounds. In the case of the ferrocyanides the stabilising ferrocyanide ions decompose on longer exposure making the sols unstable towards electrolytes. The first effect of light is to increase the degree of hydrolysis of the sulphide, the ferrocyanides and other easily hydrolysable sols and hence increases their stability towards electrolytes. This effect is more than counterbalanced by the oxidation or the decomposition of the stabilising ion on longer exposure rendering the sols unstable towards electrolytes and their subsequent coagulation on long exposure.

Our experimental results show that in general the effect of light on sols is in the same direction as that of ageing. The light effect seems more pronounced than the time effect.

The measurements of extinction coefficients of sols as recorded in this paper do not warrant any definite conclusion regarding the absorptive power of exposed and unexposed sols. Further work in this line is in progress in this laboratory.

Summary.

1. Sols of stannic hydroxide, aluminium hydroxide, thorium hydroxide and mercuric sulphide become unstable towards mono- and bi-valent ions on exposure to light.

2. Arsenious sulphide, antimony sulphide, uranium ferrocyanide and cupric ferrocyanide when exposed to light for a short time become stable in their coagulation by electrolytes; but on longer exposure they become unstable.

3. On prolonged exposure sols of antimony sulphide, mercuric sulphide and uranium ferrocyanide coagulate completely.

4. Exposed sols of stannic hydroxide, aluminium hydroxide, thorium hydroxide, mercuric sulphide, antimony sulphide and arsenious sulphide are more electrically conducting than the respective unexposed sols.

5. Measurements of extinction coefficients of sols show that in some cases the exposed sols show more absorption of light than the unexposed ones. No general conclusion can be arrived at regarding light absorption of sols on exposure to light.

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Received March 4, 1939

On the Ignition Temperature of Some Gases.

By Hemendra Kumar Sen and Harendra Nath Chatterjee.

Whilst one of us (H.K.S.) was called upon to investigate a basement explosion some time ago, our attention was drawn to an interesting work of McDavid (*J. Chem. Soc.*, 1917, **111**, 1003) who determined the ignition temperatures of a few gas mixtures by enclosing them in soap bubbles and touching them by means of a heated block or glowing spiral. The great divergence between the results obtained by McDavid and those by others is no doubt due to the method followed by individual workers to cause the ignition, and the irreproducibility of his own figures using different sources of ignition clearly indicates the futility of attempting to establish ignition temperature as a physical constant. From the practical point of view, however, the stationary method of ignition, as introduced in McDavid's work, is of considerable importance, but the determination of the lowest ignition temperatures under such circumstances is of still greater consequence. The present work has been, therefore, confined to the investigation of this latter point by firing gas mixtures enclosed in soap bubbles of different dimensions.

The difficulty, if not the impossibility, of obtaining reproducible results will appear clearly from a general consideration of the the phenomenon of ignition. The true temperature of ignition may be defined as that "at which the reaction proceeds at a rate just sufficient to overbalance the loss of heat by radiation, conduction and convection from the burning layer of gases, so that the next layer is put in the same state and a steady combustion proceeds." It would appear from this enunciation how uncertain the temperature of ignition may be depending, as it does, on the various factors referred to above. For instance, the amount of radiation depends on the difference of temperature to which the soap bubble is brought before explosion and the temperature of the surroundings. Under increasingly insulated condition, therefore, the ignition temperature would decrease. The soap bubble method introduces, in addition to the factors mentioned

above, a dividing layer of steam between the source and the inflammable mixture. Under certain conditions either of the soap bubble or of the source, the magnitude of this dividing steam layer is infinitely small, but as will be shown in the experimental part, when the dividing layers assume any considerable magnitude, a corresponding difference in the ignition temperature is noticed. The effect of this " steam cushion " is to reduce the temperature which actually reaches the inflammable mixture. It is only rational, therefore, to expect under such circumstances ignition at a somewhat higher temperature of the source. All these factors may be included in what is termed as the preflame condition, the time-lag not excepted. In our experimental determinations the time-lag has been assumed to be absent as the explosion is instantaneous. The magnitude of the error that would be caused by slight time-lags can be realised from the latest experiments of Dixon in his new concentric tube apparatus (*Trans. Faraday Soc.*, 1926, **22**, 267).

TABLE I.

(*a*) *Ignition Temperatures of Hydrogen at Atmospheric Pressure.*

Lag (seconds). ...	0·5	1·5	2·0	5·0	10·0
In air (°C). ...	630	619	605	588	577
In oxygen (°C) ...	625	618	606	588	575

(*b*) *Ignition Temperature of Methane at Atmospheric Pressure.*

Lag (seconds). ...	0·5	0·6	1·0	2·0
In air (°C). ...	—	746	728	710
In oxygen (°C) ...	670	676	657	641

This feature of instantaneous explosion fundamentally differentiates McDavid's or our results from those of others, apart from the method of ignition. Further, on all other modes of ignition, the preflame condition exercises a more conspicuous influence than on ours.

The temperature of ignition was calculated in the same way as by McDavid, only a greater accuracy was aimed at. The source of ignition was produced in the following way: Silica or mica strips were wound round with platinum wires of different lengths and diameters. The coil was uniformly wound and heated

by a number of storage cells. The heating current was regulated by a rheostat, and an ammeter in the circuit indicated the constancy of the current. The relation between the current and the temperature was determined by placing minute crystals of well-purified salts and noting the exact currents required to attain the melting points of the salts. The salts used were potassium iodide (m.p. 687°), potassium bromide (m.p. 723°) and sodium chloride (m.p. 800°). The points so obtained were on a straight line, affording thus the means of finding out other temperatures with other values of the current (Fig. I).

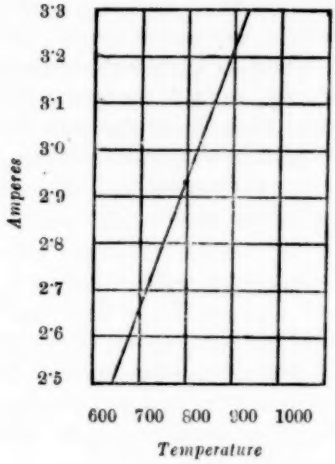

Fig. I.

The reliability of such sources, with a little practice, was quite astonishing, as we could work for hours together with the same source without any alteration in its initially calibrated values. The ammeter employed in our experiments could read up to 0·025 ampere on the scale and 0·01 by means of the eye which latter corresponded usually to 3°—4°C. An error of 0·01 ampere in the reading introduced an error of 0·5-0·7% in the ignition temperature determination.

When the form of the source was altered to that of a simple loop of platinum wire or that of a sharply bent angle, the temperatures of ignition were found to be lowest in our series of experiments. The method of calibration was as usual.

The ignition temperatures of various mixtures of hydrogen and oxygen deserve special consideration in view of numerous ignition temperatures already recorded of such mixtures. Falk (*J. Amer. Chem. Soc.*, 1906, **28** 1517; 1907 **29**, 1537) found by igniting mixtures of hydrogen and oxygen by adiabatic compression that the lowest ignition temperature is possessed by a mixture in which the two gases are in equimolecular proportions. From this he infers that the most active mixture is given by (H_2+O_2) and not by $(2H_2+O_2)$, and concluded that in all hydrogen-oxygen combustions, hydrogen peroxide is first formed. He, therefore, considers the reaction between hydrogen and oxygen to be bimolecular which requires the active masses to be equimolecular for maximum velocity. Falk's experiments were conducted under high pressures (35-40 atmos.). Dixon, who repeated Falk's experiments after introducing several changes in the apparatus (*J. Chem. Soc.*, 1914, **105**, 2036), found that with increasing proportions of oxygen, the ignition temperature of the oxy-hydrogen mixture decreases, but does not confirm that (H_2+O_2) is the most active mixture as would be seen below.

TABLE II.

Composition.	Temp.	Composition.	Temp.
$15H_2+O_2$	762°	$2H_2+O_2$ ...	526°
$10H_2+O_2$	676°	$2H_2+2O_2$	511°
$6H_2+O_2$	602°	$2H_2+8O_2$	478°
$4H_2+O_2$	561°	$2H_2+16O_2$	472°
$3H_2+O_2$	544°		

In our experiments two sets of results have to be considered in this connection: one, when the ignition source is a spiral and the other when the igniting source is a point. With a spiral, $(2H_2+O_2)$ is found to ignite at the lowest temperature, whereas with a point source, $(2H_2+3O_2)$ ignited at the lowest temperature. The idea of determining the most active mixture from the lowest ignition temperature does not, therefore, seem to be at all reliable. This is also to be inferred from the divergence in results obtained by Falk and Dixon, both of whom used the adiabatic compression method, and as such, from thermodynamic considerations, the possibility of hydrogen peroxide formation was more to be expected.

It seems probable, however, that up to a certain extent, increment in the proportion of oxygen lowers the ignition temperature. With a proportionately large source of ignition, the electrolytic mixture ($2H_2 + O_2$) ignites at the lowest temperature, and hence under that condition the maximum velocity of reaction would also correspond to a trimolecular reaction. This view would confirm Bodenstein's results who investigated the order of reaction between hydrogen and oxygen, leading their mixture into a red-hot porcelain tube, and concluded the reaction to be of the third order (*Z. physikal. Chem.*, 1899, **29**, 665). Rowe (*Z. physikal. Chem.*, 1907, **59**, 41), on recalculating Bodenstein's results, found the constants to agree just as well for a bimolecular as for a trimolecular reaction. He assumes, however, that since H_2O_2 is decomposed with very great rapidity at higher temperatures, it is incapable of being formed at all at these temperatures and that the reaction is therefore trimolecular. Fresh investigations to elucidate this point is in progress. It is noteworthy that the electrolytic gas ignites at the lowest current strength (temperature) whether platinum wire is wound on silica, porcelain or glass. In all these instances with increased proportion of oxygen the ignition temperature at first falls reaching the minimum at the electrolytic gas mixture, and again increasing with a rise in the percentage of oxygen. Using mica strips, however, for winding the wire around, the results are anomalous—with increased proportions of oxygen without passing through a minimum the ignition temperature rises. These results are shown clearly in Fig. 3. It has to be remarked, however, that the reproducibility of the above results requires some care and practice. It is hoped that by conducting experiments under more standardised conditions the soap bubble method would lend itself to greater quantitative accuracy seeing that our results are more concordant and more reproducible than those of McDavid's.

The subject is being further investigated from the point of view of the catalytic influence of the glowing wire on ignition temperature.

Experimental.

The soap solution employed in these experiments was prepared according to the method of C. V. Boys ("Soap Bubbles.") The solution was usually left in the dark for a week before use, which considerably improved its capacity of yielding larger bubbles.

The experimental arrangement is shown in Fig. II. The bubble produced at the mouth of the thistle funnel was brought in contact with the heated spiral or point, when instantaneous explosion was noticed at the requisite temperature. The experiments were conducted in a darkened room in order to be able to observe the appearance of the flame and to prevent any draught. The tables below give the results of a few of the large number of closely agreeing experiments with bubbles of twenty c.c. volume.

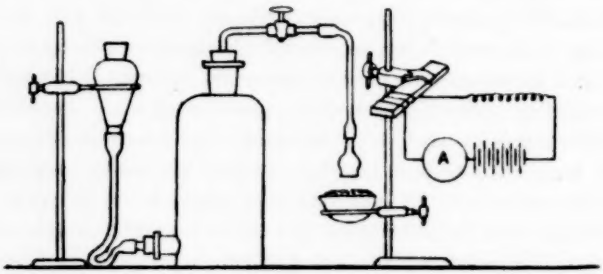

FIG. II.

TABLE III.

Diameter of Pt wire.	Length of Pt wire.	Ammeter reading.	Ignition temperature.	Composition of gas mixture (by vol).
0·3 mm.	16" (on silica)	2·84	767°	$1H_2$: $1O_2$
,,	,,	2·83	763°	$2H_2$: $1O_2$
,,	,,	2·81	756°	,, (Larger bubble 60 c. c.)
,,	,,	2·84	767°	$5H_2$: $1O_2$
,,	,,	2·9	788°	$2H_2$: 5Air
,,	,,	2·91	792°	$1H_2$: 3 ,,
,,	,,	2·87	777°	$1H_2$: 1 ,,
,,	,,	3·22	900°	1CO : 1 ,,
,,	,,	3·18	886°	2 ,, : 1 ,,
,,	,,	3·225	902°	2 ,, : $1O_2$
,,	,,	3·29	925°	1 ,, : 1 ,,
,,	,,	3·21	897°	3 ,, : 1 ,,
,,	,,	3·16	879°	1 Coal gas : 1 air.
,,	,,	3·04	837°	2 ,, ,, 1 ,,

TABLE IV.

Diameter of Pt wire.	Length of Pt wire.	Ammeter reading.	Ignition temperature.	Composition of gas mixture (by vol.)
0·3 mm.	6″ (on silica)	3·35	762°	$1H_2$: $1O_2$
,,	,,	3·33	758°	2,, : 1,,
,,	,,	3·34	760°	5,, : 1,,
,,	,,	3·67	846°	2CO : 1,,

TABLE V.

0·3 mm.	16″ (on mica)	3·05	750°	$1H_2$: $1O_2$
,,	,,	3·025	742°	,, (Bigger bubble 60 c. c.)
,,	,,	3·02	740°	$2H_2$: $1O_2$
,,	,,	3·00	733°	,, (Bigger bubble 60 c.c.)
,,	,,	3·04	747°	$5H_2$: $1O_2$
,,	,,	3·43	882°	2CO : 1,,
,,	,,	3·37	862°	,, (Bigger bubble 60 c.c.)

TABLE VI.

(*Point source*)

0·3 mm.	3″	3·27	687°	$2H_2$; $1O_2$
,,	,,	2·95	537°*	,, (Bigger bubble 60 c. c.)
,,	,,	3·61	843°	2CO : $1O_2$
,,	,,	3·48	783°	,, (Bigger bubble 60 c. c.)

TABLE VII.

(*Loop source*).

Diameter of Pt wire.	Length of Pt wire.	Ammeter reading.	Ignition temperature.	Composition of gas mixture (by vol.)
0·3 mm.	3″	3·32	683°	$2H_2$: $1O_2$
,,	,,	3·1	609°	,, (Bigger bubble 60 c. c.)

* Dixon and Crofts obtained by the adiabatic compression method an ignition temperature as low as 526° for the electrolytic gas mixture. The point source scarcely glowed, yet with larger bubbles there was explosion.

TABLE VIII.

Diameter of Pt wire.	Length of Pt wire.	Ammeter reading.	Ignition temperature.	Vol. of H_2	Vol. of air.
0·25 mm.	22·5″ (on silica)	2·27	785°	1	1
,,	,,	2·29	792°	2	3
,,	,,	2·30	797°	1	3
,,	9″ (on mica)	2·50	726°	1	1
,,	,,	2·52	732°	2	3
,,	,,	2·54	740°	1	2
,,	,,	2·57	750°	1	3
,,	5″ (on mica)	2·59	709°	1	1
,,	,,	2·64	725°	1	2
0·3 mm.	21·5″ (on silica)	2·80	781°	1	1
,,	,,	2·825	788°	2	3
,,	,,	2·85	796°	1	3

TABLE IX.

Ignition of oxy-hydrogen mixtures by means of an electrically heated platinum point.

Gas-composition, (H_2 : O_2 by vol.).	Amperes. (*a*)	Amperes. (*b*)	Amperes. (*c*)
8 :2	3·25	3·42	3·325
7 :3	3·20	3·30	3·26
6·6 :3·3	3·15	3·25	3·21
6 :4	3·12	3·15	3·02
5 :5	2·98	3·05	2·9
4 :6	2·92	2·92	2·85
3 :7	3·15	3·03	2·92
2 :8	3·22	3·20	3·17

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TABLE X.

Sources of ignition.

Composition.	Pt wire wound on silica.			Pt wire wound on mica.		Pt. wire wound on porcelain.	Pt wire wound on glass.
$H_2 : O_2$	Amp.			Amp.		Amp.	Amp.
	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)		
8 :2	2·925	2·89	2·785	2·64	2·65	3·03	3·3
7 :3	2·9	2·88	2·775	2·66	2·67	3·02	3·29
2 :1	2·895	2·87	2·77	2·67	2·68	3·01	3·285
6 :4	2·9	2·91	2·78	2·68	2·685	3·02	3·29
5 :5	2·91	2·93	2·79	2·695	2·69	3·025	3·3
4 :6	2·925	2·96	2·8	2·725	2·7	3·035	3·315
3 :7	2·96	2·985	2·81	2·74	2·72	3·05	3·325
2 :8	3·02	3·01	2·83	2·76	2·77	3·06	3·345

These results are plotted below:

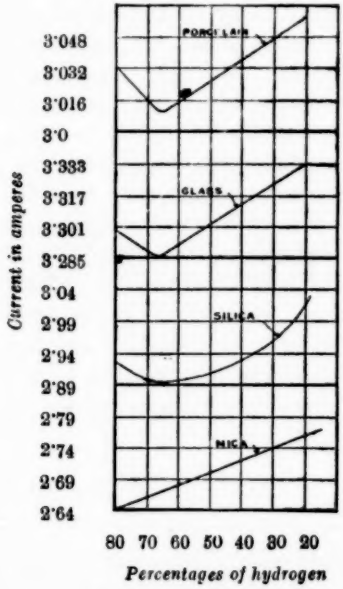

FIG. III.

TABLE XI.

The effect of size of the bubble on the ignition temperature, point source being employed in these experiments.

Composition of gas (H_2 : O_2 by vol.).	1 : 1	1 : 1	1 : 1	1 : 1
Vol. of the bubble in c. c.	60	50	30	20
Amperes.	2·66	2·73	2·79	2·82

This would indicate that size of the bubbles must be the same for obtaining reproducible and comparable ignition temperatures. Whether the lowering of the ignition temperatures with the increase in volume is due to the increasing thinness of the film or due to insulation considerations (*loc. cit.*) is at present not clear.

Summary and Conclusion.

(1) With decreasing length of wire, the ignition temperature decreases.

(2) The lowest ignition temperature is found with a point-source. There is a close agreement between this ignition temperature with large bubbles and the adiabatic ignition temperature.

(3) The larger bubbles give lower ignition temperatures due probably to the extremely thin film or to a more insulated condition of the inner gas mass.

(4) Mica being less conducting than silica, the ignition temperatures with mica strips are distinctly lower.

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Chemical Reactions in Infra-red Radiations (7304 Å).

By A. K. Bhattacharya and N. R. Dhar.

Very few chemical reactions have been investigated in presence of infra-red radiations, and the majority of photochemical changes studied are under the influence of radiations of short wave-lengths.

In these laboratories (compare Bhattacharya and Dhar, *Z. anorg. Chem.*, 1928, **175**, 357; *J. Indian Chem. Soc.*, 1929, **6**, 143) we have investigated the kinetics, temperature coefficients and quantum efficiency of several chemical reactions under the influence of radiation of mean wave-length 7304 Å. In this communication we are recording our results and conclusions on the velocity of chemical reactions in infra-red radiation.

The kinetics of the reactions have been determined in the dark and in radiation of wave-length 7304 Å at different temperatures and the quantum efficiency has been measured in the same region. The source of light was a 1000 Watt gas-filled tungsten filament lamp operated at 4·6 amperes. The lamp was placed in a box and an electric radiator was worked at the back of the lamp in order to keep it cool. Two big lenses were placed between the light source to obtain parallel light. To isolate different wave-lengths of spectral region a set of gelatin film filters (Wallace M and S) were used. The radiomicrometer was placed at a distance of one metre from the light source. Water at a constant temperature from a thermostat was circulated round the reaction vessel, which is a silica cube.

The changes in the reactions studied were determined either by suitable titrations or spectrophotometric measurements.

The following are the experimental results.

Bleaching of M/7176-neocyanin by Air at 40°.

Time in minutes	...	0	50	92	135	185
Extinction coefficient	...	0·70	0·61	0·54	0·48	0·42
k_1 (Monomolecular)	...	—	0·00119	0·00122	0·00121	0·00119 Mean 0·0012

Other results are summarised in the following tables, where

$$k_1 = \frac{1}{t} \log \frac{a_o}{a_o - x} \qquad \text{(Monomolecular)};$$

$$k_{\frac{1}{2}} = \frac{2}{t} \left[a_{\frac{1}{2}} - (a-x)_{\frac{1}{2}} \right] \qquad \text{(Semimolecular)};$$

$$k_o = \frac{x}{t} \qquad \text{(Zeromolecular)}.$$

In some of the reactions involving iodine as one of the reactants, the order of the light reaction is semimolecular whilst in the dark it is unimolecular. In these cases, in order to get comparable values, the dark reaction velocities have also been calculated according to the semimolecular formula.

Results.

Region :—$\lambda = 7608$Å$ - 7000$Å; $\lambda = 7304$Å (Mean).

Temperature.	Velocity of reaction in $\lambda = 7304$Å.	Velocity of reaction in the dark.	Temp. coeff. of the dark reaction.	Temp. coeff. of the reaction in light ($\lambda = 7304$Å) after deducting the dark reaction.	Quantum efficiency.
		Bleaching of M/7176-neocyanin by air.			
	k_1	k_1			
20°	0·00102				1·1
				1·12	
30°	0·00114	Negligible.	—		2·1
				1·05	
40°	0·00120				3·1
		Bleaching of M/24166-dicyanin.			
25°	0·00309	0·00099			0·29
			—	—	
30°	0·00340	0·00127			0·66
			1·354	1·056	
40°	0·00897	0·00172			0·89
		6·75N-Citric acid and N/44·4-chromic acid, 10 c.c. each.			
24°	0·000487	0·000359			1·5
			3·73	2·89	
34°	0·00171	0·00134			4·2
			3·65	2·75	
44°	0·00587	0·00485			5·2

Temperature.	Velocity of reaction in $\lambda = 7304$ Å.	Velocity of reaction in the dark.	Temp. coeff. of the dark reaction.	Temp. coeff. of the reaction in light ($\lambda = 7304$ Å) after deducting the dark reaction.	Quantum efficiency.
	N/4·72-*Lactic acid and N*/44·4-*chromic acid*, 10 *c.c. each.*				
	k_1	k_1			
22°	0·00120	0·00108			1·8
			1·8	1·75	
32°	0·00216	0·00195			3·2
			1·75	1·70	
42°	0·00377	0·00341			4·6
	N/4·27-*Tartaric acid and N*/44·4-*chromic acid*, 10 *c.c. each.*				
22°	0·00154	0·00143			5·6
			2·13	2	
32°	0·00327	0·00305			8·3
			2·04	1·95	
42°	0·00664	0·00621			11·0
	N/5-*Oxalic acid and N*/111-*chromic acid*, 10 *c.c. each.*				
20°	0·00335	0·00273			2·6
			1·9	1·76	
30°	0·00627	0·00518			4·1
			1·81	1·67	
40°	0·0112	0·00938			50
	N/19·47-*Oxalic acid and N*/421·3-*chromic acid* + *N*/337-$MnSO_4$ + *N*/2·78-H_2SO_4.				
	k_0	k_0			
21°	0·195	0·147			3
			2·94	1·42	
31°	0·504	0·434			9·5

Temperature.	Velocity of reaction in $\lambda=7304$Å.	Velocity of reaction in the dark.	Temp. coeff. of the dark reaction.	Temp. coeff. of the reaction in light ($\lambda=7304$Å) after deducting the dark reaction.	Quantum efficiency.
		N/89-Quinine sulphate in N/2-H_2SO_4 and N/80·88-chromic acid in 1·31N-H_2SO_4.			
	k_1	k_1	$k_{35}°/k_{25}°$		
25°	0·000232	0·000201			2·3
30°	0·000295	0·000262	1·6	1·4	0·45
35°	0·000365	0·000326			2·58
		N/4·69-Sodium lactate and N/100-iodine, 10 c.c. each.			
20°	0·000797	0·000720			3·97
			2·49	2·21	
30°	0·00196	0·00179			6·52
			2·31	2·06	
40°	0·00449	0·00414			8·38
		N/5·12-Sodium malonate and N/100-iodine, 10 c.c. each.			
20°	0·00287	0·00227			9·8
			2·21	2	
30°	0·00623	0·00503			1·24
			2·16	1·92	
40°	0·0132	0·0109			13·6
		N/2·42-Sodium tartrate and N/100-iodine, 10 c.c. each.			
20°	0·000451	0·000378			4·2
			2·51	2·26	
30°	0·00113	0·000948			7·1
			2·49	2·18	
40°	0·00272	0·00236			9·6

Temperature.	Velocity of reaction in $\lambda=7304$Å.	Velocity of reaction in the dark.	Temp. coeff. of the dark reaction.	Temp. coeff. of the reaction in light ($\lambda=7304$Å) after deducting the dark reaction.	Quantum efficiency.
		N/8-Sodium malate and N/125-iodine, 10 c.c. *each.*			
	$k_{\frac{1}{2}}$	k_1			
30°	0·00417	0·000949			15
			1·61	1·57	
40°	0·00612	0·00153			5·6
		N/5·76-Sodium citrate and N/100-iodine, 10 *c.c. each.*			
23°	0·00831	0·00115	1·63	1·63	2·6
33°	0·0148	0·00188			11·2
		N/7·17-Sodium formate and N/111·4-iodine and N/4·44-sodium acetate.			
20°	0·0132	0·0097	4·3	4·0	54
30°	0·0557	0·0417			110
		N/0·25-Potassium oxalate and N/113·6-iodine.			
				$k_{30°}/k_{20°}$	
20°	0·00368				3·7
30°	0·0131	Negligible.	—	3·56	7·5
36°	0·0256				74
		N/6·06-Ferrous sulphate and N/90·92-iodine and N/3-H_2SO_4.			
24·5°	0·00358	0·000373	$k_{34·5}/k_{24·5°}$		8·34
30°	0·00903	0·000675	2·92	2·85	14·2
34·5°	0·0128	0·00110			52·7
		N/1·5-Sodium nitrite and N/32-iodine and N/6-CH_3·COONa.			
20°	0·00772	0·000353	k_{30}/k_{20}		32
25°	0·0136	0·000574	2·71	2·61	66
30°	0·0220	0·000955			77

Temperature.	Velocity of reaction in $\lambda=7304A°$.	Velocity of reaction in the dark.	Tem. coeff. of the dark reaction.	Temp. coeff. of the reaction in light ($\lambda=7304A°$) after deducting the dark reaction.	Quantum efficiency.
		49% -*Acetone and N/50-iodine* + *N/9·42-HCl.*			
	k_0	k_0			
21°	0·0701	0·0650	3·21	2·94	3·6
31°	0·224	0·209	3·0	2·87	11·2
41°	0·672	0·629			23·8
		43% -*Methyl alcohol and N/101·7-bromine, 10 c.c. each.*			
	k_1	k_1			
20°	0·00453	0·00325	2·5	2·42	3·65
30°	0·0111	0·0080	2·45	2·32	6·8
40°	0·0269	0·0196			16·7
		25% -*Ethyl alcohol and N/113·7-bromine, 10 c.c. each.*			
20°	0·00540	0·00465	2·84	2·67	1·1
30°	0·0152	0·0132	2·77	2·45	2·1
40°	0·0415	0·0366			3·5
		N/12·23-Rochelle salt and N/121-bromine + *N/6·6-*CH_3.COONa.			
20°	0·0133	0·00372	$k_{30°}/k_{20°}$		24·4
25°	0·0242	0·00674	3·28	2·08	26
30°	0·0321	0·0122			59
		N/250-Ferric chloride and N/50-NH_4CNS, *10 c.c. each.*			
20°	0·000284			2·5	3·4
30°	0·000709	Negligible.	—	2·3	4·6
40°	0·00163				7·3
		*N/50-Potassium persulphate and N/5-*KI.			
20°	0·00995	0·00758	1·90	1·64	5
30°	0·0183	0·0144	1·87	1·60	13·4
40°	0·0332	0·0270			28·6

Temperature.	Vilocity of reaction in $\lambda = 7304$Å.	Velocity of reaction in the dark.	Temp. coeff. of the dark reaction.	Temp. coeff. of the reaction in light ($\lambda = 7304$Å) after deducting the dark reaction.	Quantum efficiency.
		Decomposition of M/80·8-sodium cobaltinitrite.			
	k_1	k_1			
20°	0·000804	0·000589	3·5	2·7	1·1
30°	0·00266	0·00208	3·04	2·6	2·5
40°	0·00783	0·00632			6
		0·898*N*-*Sodium formate and* $N/15$-$HgCl_2$.			
20°	0·000808	0·000665	4·36	4·12	27·3
30°	0·00349	0·00290			·68
		$N/19·12$-*Oxalic acid and* $N/421·3$-$KMnO_4$ *and* $N/337$-$MnSO_4$ $+ N/2·78$-H_2SO_4.			
8·5°	0·0351	0·0220		$k_{24·5}/k_{14·5}$	39
14·5°	0·0652	0·0466	3·09	2·4	36
24·5°	0·1896	0·144			36
		$N/4·72$-*Lactic acid* (10 c.c.) $+ N/86·25$-$KMnO_4$ (5 c.c.) $+ N/69$-$MnSO_4$ (5 c.c.).			
19°	0·0196	0·0149	2·5	2·3	14
29°	0·0481	0·0373	2·48	2·08	23
39°	0·115	0·925			41
		$N/5·36$-*Tartaric acid* (10 c.c.) $+ N/98·45$-$KMnO_4$ (5 c.c.) $+ N/69$-$MnSO_4$ (5 c.c.).			
16°	0·0188	0·0140	2·46	2·3	11
26°	0·0455	0·0345	2·40	2·2	26
36°	0·107	0·0828			37

Temperature.	Velocity of reaction in $\lambda = 7304$ Å.	Velocity of reaction in the dark.	Temp. coeff. of the dark reaction.	Temp. coeff. of the reaction in light ($\lambda = 7304$ Å) after deducting the dark reaction.	Quantum efficiency
	N/5-*Citric acid* (10 c.c.) + *N*/50-$KMnO_4$ (5 c.c.) + *M*/89-$MnSO_4$ (5 c.c.).				
	k_1	k_1			
15°	0·00609	0·00473			9
25°	0·0170	0·0138	2·92	2·35	17
30°	0·0255	0·0219			28
	N/10-*Potassium oxalate* + *N*/100-*bromine* (2 gms. KBr in 100 c.c. of *N*/100-Br_2).				
20°	0·0248	0·00456			36
			5·61	3·06	
30°	0·0618	0·0256			62
			5·20	3·0	
40°	0·320	0·133			85

The foregoing results show that several chemical reactions are appreciably accelerated by radiations of wave-length 7304A° which lies in the infra-red region. We have carefully measured the extinction coefficient of the reacting substances by Nutting's spectrophotometer and have found appreciable absorption in the region $\lambda = 7000$ A°. It is apparent therefore that the reacting substances actually absorb the radiation of wave-length 7304 A° and are activated by the absorption of energy and then react chemically. We have also observed that all these reactions can be accelerated by radiations of wave-lengths 5650 A° and 4725 A° and these wave-lengths are appreciably absorbed by the reacting systems. We have measured the kinetics, temperature coefficients and quantum efficiency of several reactions in these regions as well (*cf.* Bhattacharya and Dhar, *Z. anorg. Chem.*, 1928, **175**, 357; 1928, **176**, 372).

The extinction coefficient of neocyanin shows that the radiations of wave-lengths longer than 5670A° are completely absorbed even by very dilute solutions of neocyanin (*vide* next Table). As the wave-length of the incident radiation is decreased the absorption passes

through a minimum and then increases with the decrease of wave-length. The velocity of the bleaching of neocyanin is greatest in the region $\lambda=7804$ A°, less in the region $\lambda=5650$ A° and least in the region $\lambda=4725$ A°. This shows that the velocity of reaction and absorption go hand in hand.

We have measured photographically the absorption of several of these reacting mixtures using a Hilger quartz-spectrograph with a copper arc as a source of light. With an exposure of about 2 minutes no absorption is observed with mixtures of chromic acid and organic acids in the region of wave-lengths greater than 4725 A° using panchromatic plate but our experimental results results on the velocity measurements show that these reactions are not only accelerated by radiations of wave-length 4725 A° and 5650A° which lie in the visible part of the spectrum but even by radiation of $\lambda=7304$ A°, which lies in the infra-red region. It appears therefore that small amount of absorption of incident light cannot be observed by a photographic method on short exposure. We have measured the extinction coefficients of an aqueous solution of neocyanin and mixtures of citric acid and chromic acid and the following results have been obtained.

Wave-length.	Extinction coefficient of an aqueous solution of neocyanin.	Extinction coefficient of citric acid and chromic acid.
7000 A°	Complete absorption	0·04
6707	,,	0·11
5970	Beyond scale	0·13
5670	1·96	0·16
5490	0·86	0·18
5320	0·44	0·22
5200	0·21	0·38
5000	0·24	0·52
4910	0·27	0·53
4800	0·31	0·60
4720	0·43	0·65
4670	0·48	0·91
4550	0·54	0·98
4400	0·62	1·11

Hence the extinction coefficient measurements show that all radiations from 7000 A° to 4400 A° are actually absorbed by an aqueous solution of neocyanin and the mixture of citric acid and chromic acid Similar results showing appreciable absorption of all radiations from 7000 to 4400 A° have been observed with the other reacting systems.

It is well-known that the absorption of radiation by molecules is a very complex phenomenon. A very thin layer of mercury vapour shows marked absorption of wave-length 2537 A° whilst columns of air 9·5 and 39·4 metres long respectively show feeble absorption of radiations 7600 and 6900A°. These absorptions are ascribed to oxygen of the atmosphere (compare Foote and Moher, " Origin of Spectra ", 1922, p. 89; King, *Astrophys. J.*, 1922, **55**, 411). The few exceptions of Stokes' law of fluorescence where the frequeney of emitted light is greater than the frequency of the incident radiation observed by Wood (*Phil. Mag.*, 1928, (*vii*), **6**, 310) and others with vapours of sodium, iodine and other fluorescent substances have been explained from the following point of view. In a system there are few molecules the energy of which is much greater than the energy of the average molecules. When the incident radiations falls on such an active molecule, the molecule is further activated by the absorption of incident radiation and under favourable conditions it can revert directly to the inactive state giving out radiation of greater energy content than that available from the incident radiation. Recently Raman (*Indian J. Phys.*, 1928, **2**, 399) has observed this phenomenon (anti-Stokes effect) with substances such as carbon tetrachloride and benzene when illuminated by radiation of wave-length 4304 A° which is not supposed to be absorbed but scattered by molecules of carbon tetrachloride or benzene. It is apparent therefore that there can be activating of molecules and a shift towards the shorter wave-length side even with so called scattered radiations.

Incidentally it should be mentioned that this phenomenon of shift wave-length is a measure of the number of active molecules present in a system.

After having accelerated several photochemical reaction by radiations of wave-lengths 4725 A°, 5650 A° and 7304A°, we are definitely of the opinion that all these radiations are appreciably absorbed by the reacting substances and this we have been able to prove by the measurements of extinction coefficients, though photographically no absorption is observed.

According to the radiation hypothesis of Trautz (*Z. wiss. Phot.*, 1906, **4**, 160), Perrin (*Ann. Physik*, 1919, **11**, 1) and Lewis (*J. Chem. Soc.*, 1914, **105**, 2330 ; 1915, **107**, 233) we can easily calculate from the temperature coefficient of the thermal reaction the wave-length of the radiation which should accelerate the chemical change. The following results have been obtained :

Reaction.	Temp. coefficient (dark).	Wave-length.
Decomposition of sodium cobaltinitrite	3·5	1·3μ
Acetone and iodine in presence of HCl	3·21	1·38μ
Rochelle salt and bromine	3·2	,,
Sodium formate and mercuric chloride	4·36	1·08μ
Potassium oxalate and iodine	7·2	0·86μ
Potassium oxalate and bromine	5·6	0·94μ
Sodium formate and iodine	4·3	1·09μ
Ferrous sulphate and iodine	2·92	1·46μ
Citric acid and chromic acid	3·73	1·2μ
Oxalic acid, chromic acid and manganous sulphate.	2·94	1·44μ

It is evident, therefore, that all the reactions should be accelerated by short infra-red radiation. As a matter of fact, we have observed accelerations in all the reactions investigated by us by radiation of wave-length 7304A°. We are of the opinion that the wave-lengths obtained by calculation from the thermal temperature coefficients may be regarded as the threshold limit. No acceleration of the change is possible with radiations of longer wave-lengths than the threshold limit. This point may also be made clear from another line of argument. Following Arrhenius, we know that there are active and inactive molecules in a system and that chemical changes take place between the active molecules only and it has also been

held that an increase in temperature means an increase in the number of active molecules. Now those dark reactions, which are very sensitive to the influence of temperature, are evidently the ones where the difference in energy between the active and inactive molecules is very marked. In other words, in activating the inactive molecules in such a system absorption of energy in quanta of greater energy content would be necessary than in a system where the difference in energy levels between the active and inactive molecules is not so prominent.

Dhar (*J. Chem. Soc.*, 1917, **111**, 707) has shown that fast dark reactions have smaller temperature coefficients than comparatively slow ones. This is because in a fast reaction the number of active molecules is much greater than in the slower ones. Hence a fast reaction would not be so sensitive to the influence of temperature. Thus it appears that those reactions which have small temperature coefficients in the dark could be activated by quanta of smaller energy content and consequently such reactions should be acclerated by short infra-red radiations. On the other hand, those thermal reactions which are very sensitive to the influence of temperature should be activated by radiations of larger energy quanta and hence ought to be sensitive to shorter wave-lengths.

It must be pointed out clearly that according to the views advanced in the foregoing pages we can get the threshold frequencies from the measurements of temperature coefficients of the dark reactions. Radiations of longer wave-lengths will not promote the reaction in question. The main difference between this conception and the Perrin-Lewis radiation hypothesis is that according to the latter view the wave-length calculated from the temperature coefficient should bring about the maximum speed of that reaction in question whilst according to the conception now put forward, the threshold frequency is the minimum frequency necessary for the carrying out of the reaction.

The foregoing conclusion is corroborated by the observation of Taylor and co-workers (*Trans. Faraday Soc.*, 1927, **23**, 31, 38) that the active frequencies for the combination of hydrogen and chlorine are not confined to any restricted regions, since, when light is filtered through chlorine,its photochemical effect falls rapidly not towards zero but towards a definite residual value. Thus some of the very feebly absorbed frequency must be active in the combination of hydrogen and chlorine.

From the foregoing experimental results and conclusions it will be clear that the main argument raised by Langmuir (*J. Amer. Chem. Soc.*, 1920, **42**, 2090), Polanyi (*Z. Physik*, 1920, **1**, 337; 1920, **2**, 90) and others against the radiation hypothesis of chemical change that reacting substances do not show absorption of such radiation as are obtained from the temperature coefficient of the thermal reaction seems doubtful.

Summary.

(1) The following reactions have been accelerated by radiation of wave-length 7304 A° :—(*i*) bleaching of neocyanin, (*ii*) bleaching of dicyanin; (*iii*) citric acid and chromic acid; (*iv*) lactic acid and chromic acid; (*v*) tartaric acid and chromic acid; (*vi*) oxalic acid and chromic acid; (*vii*) oxalic acid and chromic acid and manganous sulphate; (*viii*) quinine sulphate and chromic acid; (*ix*) sodium lactate and iodine; (*x*) sodium malonate and iodine; (*xi*) sodium tartrate and iodine; (*xii*) sodium malate and iodine; (*xiii*) sodium citrate and iodine; (*xiv*) sodium formate and iodine; (*xv*) potassium oxalate and iodine; (*xvi*) ferrous sulphate and iodine; (*xvii*) sodium nitrite and iodine; (*xviii*) acetone and iodine; (*xix*) methyl alcohol and bromine; (*xx*) ethyl alcohol and bromine; (*xxi*) Rochelle salt and bromine; (*xxii*) ferric chloride and ammonium thiocyanate; (*xxiii*) potassium persulphate and potassium iodide; (*xxiv*) decomposition of sodium cobaltinitrite; (*xxv*) sodium formate and mercuric chloride; (*xxvi*) oxalic acid and potassium permanganate and manganous sulphate; (*xxvii*) lactic acid and potassium permanganate and manganous sulphate; (*xxviii*) tartaric acid and potassium permanganate and manganous sulphate ; (*xxix*) citric acid and potassium permanganate and manganous sulphate; (*xxx*) potassium oxalate and bromine.

(2) The temperature coefficients of all these reactions in radiation of wave-length 7304 A° are less than those of the corresponding dark reactions. Hence radiation of wave-length 7304A° accelerates the above reactions and produces a lowering of their temperature coefficients.

(3) The quantum efficiency of all these reactions usually increases with increasing temperature.

(4) Measurements of extinction coefficients show that all radiations of wave-length from 4400 A° to 7000A° are absorbed by the

above reacting systems and thus they are accelerated by the absorption of the incident radiation.

(5) The wave-lengths obtained by calculation from the thermal temperature coefficients may be regarded as the threshold limit. No appreciable acceleration of the chemical change is possible with radiations of longer wave-lengths than the threshold limit. All radiations of frequency greater than the threshold frequency are appreciably absorbed by the reacting substances and can accelerate the reactions investigated.

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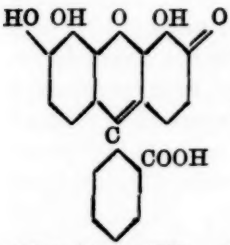
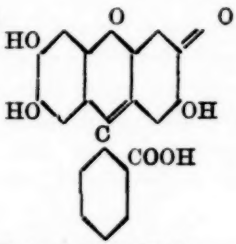
Fluoresceins and Rhodamines of the Mixed Type.

By Narendra Nath Ghatak and Sikhibhushan Dutt.

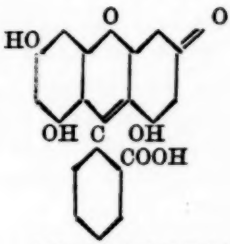
From the point of view of colour and chemical constitution, the fluoresceins and the rhodamines belong to a class of dyestuffs which offer interesting possibilities for generalisation. For example, it is possible from a study of them, to find out the influence of the position of a hydroxy or an amino group on the fluoran nucleus. It has already been pointed out by Dutt (*J. Indian Chem. Soc.*, 1927, **4**, 107) that the nearer a hydroxy group to the pyrone oxygen atom, the greater is the development of colour. Thus in alkaline(KOH) solution:



Gallein (blue) λ 5980.



Hydroxyquinol-phthalein (pink) λ 5540.



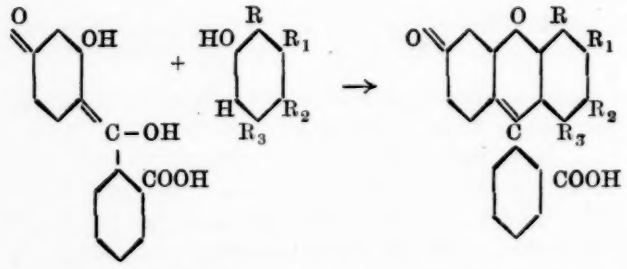
Phloroglucinol-phthalein (orange) λ 4980.

Though, of course, a large number of pyronine dyestuffs have been prepared from various dibasic acids like succinic (Dutt and Thorpe, *J. Chem. Soc.*, 1924, **125**, 2524), quinolinic (Ghosh, *J. Chem. Soc.*, 1919, **115**, 1102), naphthalic (Terisse, *Annalen*, 1885, **227**, 1102), diphenic (Dutt, *J. Chem. Soc.*, 1923, **123**, 225), camphoric (Sircar and Dutt, *J. Chem. Soc.*, 1922, **121**, 1283; and Singh, Rai and Lal, *J. Chem. Soc.*, 1922, **121**, 1421); imidazole-dicarboxylic (Tewari and Dutt, *J. Indian Chem. Soc.*, 1927, **4**, 201) and many similar acids, possessing widely different colour and dyeing properties, yet in none of these series of compounds a complete generalisation has yet been attempted regarding the chemical constitution and the colour of the substance. Besides it has been found that the effect of various acid residues on the colour of these substances is not so marked as for

example in the change from gallein to hydroxyquinol-phthalein and then to phloroglucinol-phthalein. By condensing resorcinol with these dibasic acids of various characters a number of fluoresceins are obtained, all of which possess different shades of yellow or orange colour and absorption maxima between λ4800 and λ5000, and are characterised by the intense yellow-green fluorescence which their solutions exhibit. But in none of these cases the colour change is so marked as from blue to pink and from pink to orange.

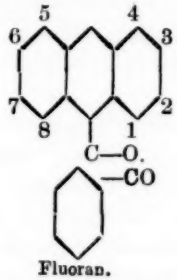
According to a theory of colour on the basis of molecular strain which has been advanced by one of the present authors (Dutt, *loc. cit.*), whenever there is an oxygen atom in a ring system, it becomes a seat of strain on account of the distortion of its normal valency directions, and therefore in the fluoran nucleus, which is the parent nucleus of all these pyronine dyestuffs, the pyrone oxygen atom is the seat of strain which essentially determines the condition of equilibrium of the dye molecule. Hence it is evident that the nearer a hydroxy or an amino group is to the oxygen atom in a dye molecule the greater will be the colour of the substance. This can be clearly seen from the table given at the end of the paper.

Mixed fluoresceins and rhodamines, *i.e.*, phthalein dyestuffs in which the substituents in the two sides of the fluoran nucleus are dissimilar, are an interesting class of dyestuffs prepared by condensing 2:4-dihydroxy benzoyl benzoic acid with aromatic hydroxy or amino-hydroxy compounds in accordance with the diagram given below:



in which R, R_1, R_2, R_3 may be H, OH, NH_2, $N(CH_3)_2$, $N(C_2H_5)_2$, etc. These dyes are interesting in view of the fact that many of them are applicable to both metallic and tannin mordanted cotton yielding brilliant fast shades. The following aromatic hydroxy and amino-hydroxy compounds have been condensed with 2:4-dihydroxy benzoyl-benzoic acid and the corresponding phthalein obtained: phenol,

o-cresol, *m*-cresol, *p*-cresol, catechol, resorcinol, quinol, thymol, carvacrol, α-naphthol, β-naphthol, 2:7-dihydroxy-naphthalene, pyrogallol, phloroglucinol, *m*-dimethylamidophenol and *m*-diethylamidophenol. The nomenclature of these compounds has been arrived at by considering them as substituted derivatives of fluoran:



Fluoran.

Most of these compounds are intensely fluorescent, and they dye silk, wool and mordanted cotton beautiful bright shades. For the sake of abbreviation the properties of these compounds are summarised in the form of a table given at the end of the paper.

In the case of several compounds described in this paper, such as those derived from phenol, *o*-cresol, *m*-cresol, thymol, α-naphthol and β-naphthol, the *ortho* as well as the *para* condensation is theoretically possible, but it has been found that in every case the *ortho* compound is invariably formed. This is probably due to the fact that only in the *ortho* condensation the fluoran nucleus which is very stable is capable of formation. That all the compounds described in this paper are derivatives of fluoran is shown by the fact that on distillation with zinc dust they all yield phenyl xanthene, m.p. 137°.

Experimental.

2:4-*Dihydroxy-benzoyl-benzoic acid*.—This was prepared according to the method of Baeyer (*Annalen*, 1876, **183**, 23) with some modification. Sodium hydroxide (160 g.) in water (80 c.c.) was maintained at 160-165°, and fluorescein (80 g.) added with vigorous stirring. The intense violet colour which at first developed gradually faded to a straw yellow colour and the completion of the reaction was ascertained when a small sample of the melt dissolved in water without any fluorescence. The melt on cooling was dissolved in water (400 c.c.)

and the dihydroxy benzoyl benzoic acid precipitated by hydrochloric acid. It crystallised from dilute alcohol in yellow shining plates melting at 201° (yield, 48 gms.).

6-*Hydroxy-fluoran*.—The dihydroxy benzoyl benzoic acid (30 g.) was heated with crystallised phenol (12 g.) and concentrated sulphuric acid (10 c.c.) for 17 hours at 140°. The excess of phenol was distilled off in steam, and the condensation product powdered, dissolved in dilute sodium hydroxide solution, filtered and reprecipitated by dilute hydrochloric acid. It was then crystallised from dilute alcohol (yield, 16 gms.).

4:6-*Dihydroxy-fluoran* obtained from 2:4-dihydroxy benzoyl-benzoic acid and catechol in a manner similar to the above, crystallised from dilute acetic acid. Yield 53%.

1:6-*Dihydroxy-fluoran*.—The condensation product with resorcinol was separated into two compounds by means of chloroform, one of which was identified to be ordinary fluorescein, while the other was isomeric with it. From the method of formation it is quite evident that this latter compound cannot be anything else but 1:6-dihydroxy-fluoran (yield, 27%, fluorescein, 63%).

2:3-*Dihydroxy-fluoran* was obtained from 2:4-dihydroxy benzoyl benzoic acid and quinol in a manner similar to the catechol compound. It crystallised from alcohol (yield, 42%).

3:4:6-*Trihydroxy-fluoran*.—A mixture of 2:4-dihydroxy-benzoyl benzoic acid (10 g.), pyrogallol (6 g.) and concentrated sulphuric acid (3 c.c.) was heated at 150° for 9 hours. The condensation product was dissolved in absolute alcohol and precipitated with petroleum ether. It was finally crystallised from glacial acetic acid (yield 50%).

1:3:6-*Trihydroxy-fluoran* was obtained from the dihydroxy-benzoyl benzoic acid and phloroglucinol in a manner similar to the above. It crystallised from glacial acetic acid (yield, 65%).

4-*Methyl*-6-*hydroxy-fluoran*.—A mixture of the acid (3 g.), *o*-cresol (1·5 g.) and tin-tetrachloride (4 g.) was heated at 120° for 15 hours. The melt was extracted with dilute ammonia, filtered and the fluoran precipitated from the filtrate by acetic acid. It was then crystallised from dilute alcohol (yield, 70%).

3-*Methyl*-6-*hydroxy-fluoran* was prepared from *m*-cresol in a manner similar to the above. It crystallised from methyl alcohol. (Yield, 47%).

2-*Methyl*-6-*hydroxy-fluoran* was prepared from 2:4-dihydroxy-benzoyl-benzoic acid and *p*-cresol by using concentrated sulphuric acid

instead of tin-tetrachloride as condensing agent. It crystallised from dilute alcohol (yield, 53%).

1-*Methyl*-4-iso*propyl*-6-*hydroxy-fluoran*.—The acid (3 g.) and thymol (2 g.) were heated together at 135° for 16 hours without the use of any condensing agent. Any unchanged thymol was distilled off in steam, and the condensation product dissolved in dilute sodium hydroxide, filtered and reprecipitated with acetic acid. It was then crystallised from alcohol (yield, 40%). The use of a condensing agent lowers the yield and makes the compound more difficult to purify.

1-iso*Propyl*-4-*methyl*-6-*hydroxy-fluoran* was obtained from the acid and carvacrol in a manner similar to the above with the exception that a few drops of concentrated sulphuric acid were used as the condensing agent. It crystallised from dilute alcohol (yield, 46%).

3:4-*Phenylene*-6-*hydroxy-fluoran*.—A mixture of the acid (3 g.), α-naphthol (2 g.) and cencentrated sulphuric acid (3 g.) was heated at 120° for 8 hours. The product was powdered, dissolved in dilute sodium hydroxide, filtered and reprecipitated with dilute hydrochloric acid. It crystallised from acetic acid (yield, 41%).

2:3-*Phenylene*-6-*hydroxy-fluoran*.—It was prepared from the acid and β-naphthol in a manner similar to the above. It crystallised from dilute alcohol (yield, 40%).

2:3-(4′-*Hydroxy*)-*phenylene*-6-*hydroxy-fluoran* was prepared from the acid and 2:7-dihydroxy-naphthalene in a manner similar to the above. It crystallised from dilute alcohol (yield 38%).

3-*Dimethylamido*-6-*hydroxy-fluoran*.—A mixture of the acid (10 g.), *m*-dimethylamido-phenol (6 g.) and concentrated sulphuric acid (1·5 g.) was heated at 125° for 10 hours. The product was powdered and extracted with alcohol. The alcoholic extract on dilution with water gave a precipitate of the fluoran which was subsequently recrystallised from benzene (yield 43%.)

3-*Diethylamido*-6-*hydroxy-fluoran* was obtained from the acid and *m*-diethylamido-phenol in a manner similar to the above. It crystallised from dilute alcohol (yield, 51%).

Properties of the fluoresceins and the rhodamines of the mixed type.

Name. (F=Fluoran).	Appearance.	M.p.	Absorption maxima (λ).	Shade on silk and wool.	Colour of solution.	Colour of fluorescence.	Analyses. (Theoretical values in brackets).
6-Hydroxy-F	... Yellow needles	181°	4930	Light yellow	Bright yellow	Yellow-green	C=75·3(75·9); H=4·1(3·8)%.
4 : 6-Dihydroxy-F	... Yellowish-grey needles.	179°	4950	Light brown	Brownish yellow	,, ,,	C=71·9(72·3); H=3·8(3·6)%.
1 : 6-Dihydroxy-F	... Bright yellow needles.	Above 280°	4930	Brown-yellow	Orange yellow	,, ,,	C=72·1(72·3); H=4·0(3·6)%.
2 : 6-Dihydroxy-F	... Yellow needles.	177°	4920	Pale yellow	Yellow	,, ,,	C=72·1(72·3); H=4·0(3·6)%.
3 : 4 : 6-Trihydroxy-F	Brick-red ,,	189°	4950	Greyish brown	Dirty brown	... ...	C=68·6(68·9); H=3·5(3·4)%.
1 : 3 : 6-Trihydroxy-F	Orange-red ,,	Above 285°	4940	Orange-yellow	Blood red	... ...	C=68·7(68·9); H=3·5(3·4)%.
4-Methyl-6-hydroxy-F	Yellow ,,	135°	4935	Pale yellow	Yellow	Yellow-green	C=76·3(76·4); H=4·3(4·2)%.
3-Methyl-6-hydroxy-F	,, ,,	143°	4935	,, ,,	,,	,, ,,	C=76·1(76·4); H=4·1(4·2)%.
2-Methyl-6-hydroxy-F	,, ,,	152°	4935	,, ,,	,,	,, ,,	C=76·2(76·4); H=4·4(4·2)%.
1-Methyl-1-*iso*propyl-6-hydroxy-F.	Deep yellow ,,	166°	4945	Bright yellow	Orange-yellow	,, ,,	C=77·1(77·4); H=5·6(5·4)%.

1-*iso*-Propyl-4-methyl-6-hydroxy-F.	,,	,,	134°	4940	,, ,,	,, ,,	,, ,,	C=77·0(77·4); H=5·7(5·4)%.
3 : 4-Phenylene-6-hydroxy-F.	Orange-red	,,	117°	4945	Orange-yellow	Orange-red	Moss-green	C=78·3(78·7); H=4·1(3·8)%.
2 : 3-Phenylene-6-hydroxy-F.	,,	,,	113°	4945	,, ,,	,, ,,	,, ,,	C=78·4(78·7); H=3·9(3·8)%.
2 : 3-(4′-Hydroxy-) phenylene-6-hydroxy-F.	Brownish-red	,,	183°	4960	Light brick-red	Brownish red	,, ,,	C=75·1(75·4); H=3·9(3·7)%.
3-Dimethylamido-6-hydroxy-F.	Pink	,,	169°	5490	Bright pink	Pink	Yellow-brown	C=73·3(73·5); H=4·9(4·7)%.
3-Diethylamido-6-hydroxy-F.	Reddish-violet	,,	163°	5500	Crimson	Reddish-violet	,, ,,	C=74·1(74·4); H=5·8(5·4)%.

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Influence of Intensity on the Velocity of Photochemical Reactions.

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In publications (Bhattacharya and Dhar, *Z. anorg. Chem.*, 1928, **169**, 381 ; 1928, **175**, 357; Mukerji and Dhar, *Z. Elektrochem.*, 1926, **32**, 501; *J. Phys. Chem.*, 1928, **32**, 1308) from these laboratories we have investigated the influence of the variation of intensity of the incident radiation on the velocity of several photochemical reactions. By changing the diameter of the aperture of an Iris diaphragm, the amount of light falling on the reaction vessel and hence the intensity was varied. In all the reactions the velocities in the dark were deducted from the total change observed in light in order to get the velocity in light alone. The changes in the concentrations of the reacting substances were determined either by suitable titrations or spectrophotometric measurements. The diameters of the aperture of the Iris diaphragm used were 2 cm., 0·8 cm. and 0·4 cm. in most of the reactions. The intensity of light was taken to be directly proportional to the area of the aperture through which the light passed before falling on the reaction vessel.

The source of light in most reactions was a 1,000 watt gas-filled tungsten-filament lamp operated at 4·6 amperes. In some reactions sunlight was also utilized, whilst in others light-filters were used. The reactions investigated in these laboratories may be roughly classified in the three following groups:—

(1) Velocity tends to be proportional to the square of the incident radiation.

(2) Velocity is almost directly proportional to the intensity.

(3) Velocity becomes nearly proportional to the square-root of the intensity of the incident radiation.

From our investigations with more than forty photochemical reactions we infer that the velocities of the majority of the reactions investigated in these laboratories are proportional to the square-root of the incident radiation. Hence we have come to the conclusion that the velocities of really photochemical reactions are proportional to the square-root of the intensity of the incident radiation.

We have advanced the view that the two important factors,

which are of consequence in the relation between intensity and the velocity of a reaction, are—

(*a*) The amount of absorption of the incident radiation by the reacting system.

(*b*) The acceleration of the reaction in presence of light.

When the absorption of radiation is high and the reaction is not markedly photochemical in nature and the velocity of the reaction in the dark is appreciable, direct proportionality or even square of intensity is likely to be observed. On the other hand, when the reaction is highly photochemical in nature and the velocity of the dark reaction is practically negligible, square-root relationship will be expected.

It will be evident, therefore, from the foregoing lines that if a reaction, which is proportional to the square of the intensity of the incident radiation, can be greatly accelerated by the incidence of strong light, it should show a tendency to follow the direct or square-root relationship. On the other hand, reaction following the square-root relationship can be made to be proportional directly to the intensity, if the dark velocity of such a reaction can be greatly accelerated and the reacting system is exposed to radiation which is not intense and slightly absorbed by the reacting system.

We have been successful in changing the relationship between the intensity and velocity by changing the velocity of the dark reaction and the intensity and quality of the incident radiation in the following reactions :—

1. Potassium oxalate and iodine.
2. Rochelle salt and bromine.
3. Quinine sulphate and chromic acid.
4. Sodium formate and iodine.

Dhar (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1084) was the first to investigate the kinetics of the reaction between potassium oxalate and iodine in the light and in the dark, and he found that the velocity of the reaction is greatly accelerated by light, and it is greater in sunlight than in diffused light. Later on Berthoud and Bellenot (*Helv. Chim. Acta*, 1924, **7**, 307) investigated the same reaction and found it to be proportional to the square-root of the incident radiation, and this conclusion has been supported by Briers, Chapman, and Walters (*J. Chem. Soc.*, 1926, **129**, 562). Recently Mukerji and Dhar (*J. Phys. Chem.*, 1928, **32**, 1308) observed that the reactions between potassium oxalate and iodine, and ammonium

oxalate and iodine is proportional to the square-root of the incident radiation in presence of white light obtained from a 1,000 watt gas-filled tungsten-filament lamp and also radiation of wave-length 4725 Å.

We have reinvestigated the reaction between potassium oxalate and iodine in radiations of wave-length 5650Å and 7304Å using different intensities. The previous workers dissolved their iodine in potassium iodide which is a marked retarder in the reaction. Hence in order to accelerate the dark reaction, we have avoided potassium iodide and have only used an aqueous solution of iodine. The following experimental results have been obtained.

N-Potassium oxalate and N/550-iodine (aqueous), 10 c.c. each.
Temperature = 20°.

Wave-length.	Diameter of the aperture.	$k_{\frac{1}{2}}$ Semimolecular.	$k_{\frac{1}{2}}$ After deducting the dark reaction. $k_{\frac{1}{2}}$ (*dark*) = 0·00353.
5650Å	2 cm.	0·00968	0·00615 (I)
	0·8	0·00502	0·00149 (II)
	0·4	0·00400	0·00047 (III)
7304Å	2 cm.	0·00816	0·00463 (I)
	0·8	0·00456	0·00103 (II)
	0·4	0·00382	0·00029 (III)

Wave-length.	Ratio of velocities.	If directly proportional to change in intensity.	If proportional to the square-root of the change in intensity.
5650Å	$\frac{I}{II} = 4·1$	$\frac{3·14}{0·5024} = 6·25$	$\sqrt{6·25} = 2·5$
	$\frac{II}{III} = 3·2$	$\frac{0·5024}{0·1256} = 4$	$\sqrt{4} = 2$
	$\frac{I}{III} = 13$	$\frac{3·14}{0·1256} = 25$	$\sqrt{25} = 5$
7304Å	$\frac{I}{II} = 4·5$	$\frac{3·14}{0·5024} = 6·25$	$\sqrt{6·25} = 2·5$
	$\frac{II}{III} = 3·6$	$\frac{0·5024}{0·1256} = 4$	$\sqrt{4} = 2$
	$\frac{I}{III} = 16$	$\frac{3·14}{0·1256} = 25$	$\sqrt{25} = 5$

The foregoing results show that the reaction between potassium oxalate and iodine (dissolved in potassium iodide), which is proportional to the square-root of the intensity of radiation (from a 1,000 watt gas-filled tungsten-filament lamp and of light of wave-length 4725 Å), tends to be directly proportional to the intensity of radiation of wave-length 5650 Å and 7304 Å in absence of potassium iodide. We have observed that these radiations are only slightly absorbed by the reacting system.

Mukerji and Dhar (*loc. cit.*) have shown that the velocity of reaction between Rochelle salt and bromine in presence of sodium acetate under the influence of radiation of $\lambda = 4725$ Å is practically proportional to the square of the intensity of incident radiation. Hydrogen ions markedly retard the velocity of the reaction and in order to accelerate the dark reaction we have used sodium acetate and borax.

N/13·93-*Rochelle salt* (5 c.c.) *and* N/180-*bromine* (10 c.c.) *in presence of* N/6·7-*sodium acetate* (5 c.c.).

Temperature = 20°.

Wave-length.	Diameter of the aperture.	k_1 Monomolecular.	k_1 After deducting the dark reaction.	
			k_1 (*dark*) = 0·001.	
1000 Watt lamp.	2 cm.	0·00907	0·00807	(I)
	0·8	0·00449	0·00349	(II)
	0·4	0·00275	0·00175	(III)
5650 Å (*a*)	2 cm.	0·00446	0·00346	(I)
	0·8	0·00160	0·00060	(II)
	0·4	0·00115	0·00015	(III)
	In presence of N/625-*borax.*			
			k_1 (*dark*) = 0·001.	
5650 Å (*b*)	2 cm.	0·00461	0·00361	(I)
	0·8	0·00167	0·00067	(II)
	0·4	0·00118	0·00018	(III)

In presence of N/250-*borax*.

Wave-length.	Diameter of the aperture.	k_1 Monomolecular.	k_1 After deducting the dark reaction.
			k_1 (*dark*) = 0·00172.
5650 Å (*c*)	2 cm.	0·00608	0·00436 (I)
	0·8	0·00223	0·00051 (II)
	0·4	0·00182	0·00010 (III)

In presence of N/105-*borax* .

			k_1 (*dark*) = 0·0020.
5650 Å (*d*)	2 cm.	0·00750	0·00550 (I)
	0·8	0·00262	0·00062 (II)
	0·4	0·00210	0·00010 (III)

Wave-length.	Ratio of velocities.	If directly proportional to change in intensity.	If proportional to the square-root of the change in intensity.
1000 Watt lamp.	$\frac{I}{II}=2·3$	$\frac{3·14}{0·5024}=6·25$	$\sqrt{6·25}=2·5$
	$\frac{II}{III}=2$	$\frac{0·5024}{0·1256}=4$	$\sqrt{4}=2$
	$\frac{I}{III}=4·6$	$\frac{3·14}{0·1256}=25$	$\sqrt{25}=5$
5650 Å (*a*)	$\frac{I}{II}=5·7$	$\frac{3·14}{0·5024}=6·25$	$\sqrt{6·25}=2·5$
	$\frac{II}{III}=4$	$\frac{0·5024}{0·1256}=4$	$\sqrt{4}=2$
	$\frac{I}{III}=23$	$\frac{3·14}{0·1256}=25$	$\sqrt{25}=5$
5650 Å (*b*)	$\frac{I}{II}=5·4$	$\frac{3·14}{0·5024}=6·25$	$\sqrt{6·25}=2·5$
	$\frac{II}{III}=3·7$	$\frac{0·5024}{0·1256}=4$	$\sqrt{4}=2$
	$\frac{I}{III}=20$	$\frac{3·14}{0·1256}=25$	$\sqrt{25}=$

Wave-length.	Ratio of velocities.	If directly proportional to change in intensity.	If proportional to the square-root of the change in intensity.
5650 Å (*c*)	$\frac{I}{II}=8{\cdot}5$	$\frac{3{\cdot}14}{0{\cdot}5024}=6{\cdot}25$	$\sqrt{6{\cdot}25}=2{\cdot}5$
	$\frac{II}{III}=5{\cdot}1$	$\frac{0{\cdot}5024}{0{\cdot}1256}=4$	$\sqrt{4}=2$
	$\frac{I}{III}=43{\cdot}6$	$\frac{3{\cdot}14}{0{\cdot}1256}=25$	$\sqrt{25}=5$
5650 A (*d*)	$\frac{I}{II}=9$	$\frac{3{\cdot}14}{0{\cdot}5024}=6{\cdot}25$	$\sqrt{6{\cdot}25}=2{\cdot}5$
	$\frac{II}{III}=6{\cdot}2$	$\frac{0{\cdot}5024}{0{\cdot}1256}=4$	$\sqrt{4}=2$
	$\frac{I}{III}=55$	$\frac{3{\cdot}14}{0{\cdot}1256}=25$	$\sqrt{25}=5$

Dhar (*J. Chem. Soc.*, 1917, **111**, 707) investigated the kinetics of the reaction between quinine sulphate and chromic acid in the dark and found that the reaction is greatly accelerated by light. Mukerji and Dhar (*loc. cit.*) investigated the influence of variation of intensity on this reaction in presence of sulphuric acid using the total light from a 1,000 watt gas filled tungsten-filament lamp. They observed that the reaction is proportional to the square of the incident radiation. We have re-investigated the reaction using different amounts of sulphuric acid.

M/75-*Quinine sulphate in* N/11·7-*sulphuric acid and* M/88·8-*chromic acid*, 10 *c.c. each*.

Temperature=20°. *Source*=1,000 *watt lamp*.

Diameter of the aperture.	k_1 Monomolecular.	k_1 After deducting the dark reaction. k_1 (*dark*)=0·00004.
A. 2 cm.	0·00147	0·00143 (I)
0·8	0·000357	0·000317 (II)
0·4	0·000145	0·000105 (III)

M/75-Quinine sulphate in N/2·3-sulphuric acid and M/88·8-chromic acid.

Diameter of the aperture.	k_1 Monomolecular.	k_1 After deducting the dark reaction. k_1 (*dark*) = 0·000196
B. 2 cm.	0·00463	0·00443 (I)
0·8	0·000873	0·000677 (II)
0·4	0·000346	0·000150 (III)

M/75-Quinine sulphate in 7N-sulphuric acid and M/88·8-chromic acid.

k_1 (*dark*) ≡ 0·00346.

C. 2 cm.	0·00628	0·00593 (I)
0·8	0·000959	0·000613 (II)
0·4	0·000457	0·000111 (III)

Ratio of velocities.	If directly proportional to change in intensity.	If proportional to the square root of the change in intensity.
A. $\frac{I}{II} = 4·5$	$\frac{3·14}{0·5024} = 6·25$	$\sqrt{6·25} = 2·5$
$\frac{II}{III} = 3$	$\frac{0·5024}{0·1256} = 4$	$\sqrt{4} = 2$
$\frac{I}{III} = 13·6$	$\frac{3·14}{0·1256} = 25$	$\sqrt{25} = 5$
B. $\frac{I}{II} = 6·5$	$\frac{3·14}{0·5024} = 6·25$	$\sqrt{6·25} = 2·5$
$\frac{II}{III} = 4·5$	$\frac{0·5024}{0·1256} = 4$	$\sqrt{4} = 2$
$\frac{I}{III} = 29·5$	$\frac{3·14}{0·1256} = 25$	$\sqrt{25} = 5$
C. $\frac{I}{II} = 9·7$	$\frac{3·14}{0·5024} = 6·25$	$\sqrt{6·25} = 2·5$
$\frac{II}{III} = 5·6$	$\frac{0·5024}{0·1256} = 4$	$\sqrt{4} = 2$
$\frac{I}{III} = 53·5$	$\frac{3·14}{0·1256} = 25$	$\sqrt{25} = 5.$

The reaction between sodium formate and iodine in presence of radiation of wave-length, 4725 Å has been found by Mukerji and

Dhar to be proportional to the square of the intensity of incident radiation. In order to accelerate the dark reaction a very small amount of potassium iodide was used in dissolving iodine. Both sodium acetate and borax were used as buffer solutions.

N/6·25-*Sodium formate* (5 *c.c.*) + N/204-*iodine* (10 *c.c.*) *dissolved in very little* KI *and* N/6·7-*sodium acetate* (5 *c.c.*).

Temperature = 20°. *Source* = 1000 *watt lamp.*

Diameter of the aperture.	k_1 Monomolecular.	k_1 After deducting the dark reaction.	
		k_1 (*dark*) = 0·00697.	
A. 2 cm.	0·0259	0·0190	(I)
0·8	0·0102	0·0083	(II)
0·4	0·00785	0·00088	(III)

N/6·25-*Sodium formate* (5 *c.c.*) + N/204-*iodine in little* KI (10 *c.c.*) *and* N/250-*borax.*

		k_1 (*dark*) = 0·00691.	
B. 2 cm.	0·0182	0·0113	(I)
0·8	0·0081	0·0012	(II)
0·4	0·00714	0·00023	(III)

N/6·25-*Sodium formate* (5 *c.c.*) + N/204-*iodine* (10 *c.c.*) *in* 10% KI + N/250-*borax* (5 *c.c.*).

		k_1 (*dark*) = 0·00015.	
C. 2 cm.	0·00572	0·00422	(I)
0·8	0·00290	0·00140	(II)
0·4	0·00210	0·00060	(III)

Ratio of velocities.	If directly proportional to change in intensity.	If proportional to the square root of the change in intensity.
A. $\frac{I}{II} = 5·8$	$\frac{3·14}{0·5024} = 6·5$	$\sqrt{6·25} = 2·5$
$\frac{II}{III} = 3·8$	$\frac{0·5024}{0·1256} = 4$	$\sqrt{4} = 2$
$\frac{I}{III} = 21·6$	$\frac{3·14}{0·1256} = 25$	$\sqrt{25} = 5$

	Ratio of velocities.	If directly proportional to change in intensity.	If proportional to the square root of the change in intensity.
B.	$\frac{I}{II}=9{\cdot}4$	$\frac{3{\cdot}14}{0{\cdot}5024}=6{\cdot}25$	$\sqrt{6{\cdot}25}=2{\cdot}5$
	$\frac{II}{III}=5{\cdot}2$	$\frac{0{\cdot}5024}{0{\cdot}1256}=4$	$\sqrt{4}=2$
	$\frac{I}{III}=49$	$\frac{3{\cdot}14}{0{\cdot}1256}=25$	$\sqrt{25}=5$
C.	$\frac{I}{II}=3$	$\frac{3{\cdot}14}{0{\cdot}5024}=6{\cdot}25$	$\sqrt{6{\cdot}25}=2{\cdot}5$
	$\frac{II}{III}=2{\cdot}3$	$\frac{0{\cdot}5024}{0{\cdot}1256}=4$	$\sqrt{4}=2$
	$\frac{I}{III}=7{\cdot}03$	$\frac{3{\cdot}14}{0{\cdot}1256}=25$	$\sqrt{25}=5$

In order to make sure that the absorption of radiation is proportional to the intensity of the incident radiation, we have determined the absorption of the incident radiation by a radio-micrometer. We have observed that the amount of radiation absorbed is directly proportional to the intensity of the incident radiation.

The foregoing experimental results show that by increasing the velocity of the dark reaction and exposing it to radiation which is slightly absorbed by the reacting system, a truly photochemical reaction, which is proportional to the square-root of the incident radiation or the amount of energy absorbed, becomes directly proportional to the intensity of the incident radiation or the amount of energy absorbed.

On the other hand, a photochemical reaction which is proportional to the square of the incident radiation or is directly proportional, can be made to be proportional to the square-root of the incident radiation by decreasing the dark reaction velocity and increasing the photochemical velocity.

Our experimental results and conclusions throw a flood of light on the highly controversial question of the relation between intensity and velocity in the reaction between chlorine and hydrogen. Draper (*Phil. Mag.*, 1843, **23**, 401), Mrs. Chapman (*J. Chem. Soc.*, 1924, **125**, 1521), Kornfeld and Müller (*Z. physikal. Chem.*, 1925, **117**, 242) observed that the photochemical reaction between chlorine and hydrogen is directly proportional to the intensity of the incident

radiation ; whilst Baly and Barker (*J. Chem. Soc.*, 1921, **119**, 653) showed that the velocity increases more rapidly than the intensity.

All these workers have used total light from electric bulbs. Recently Marshall (*J. Phys. Chem.*, 1925, **29**, 1453) has investigated the same problem in presence of mercury arc light.

Marshall's results show that the combination of chlorine and hydrogen in presence of mercury lamp radiation, which is more intense than the light used by previous workers, is proportional to less than the square-root of the incident radiation.

Draper, Baly and Barker and Mrs. Chapman used electrolytic gas which always contains small amounts of oxygen. Kornfeld and Müller removed oxygen from the hydrogen, but the chlorine they used may have contained a little oxygen. On considering the details of the experiments of Mrs. Chapman, and those of Baly and Barker, we are of the opinion that there was more oxygen present in Baly and Barker's experiments than in Mrs. Chapman's gas and this will be evident from fhe following llnes from Baly and Barker's paper:—" During the course of this work we encountered considerable difficulty owing to the production of oxygen in the reaction vessel."

Moreover the light intensity in the experiment of Mrs. Chapman was greater than in the case of Baly and Barker. It is well known that oxygen markedly retards the photochemical combination of hydrogen and chlorine ; hence, it appears that the photochemical reaction velocity in the experiments of Baly and Barker was not as much accelerated as that of Mrs. Chapman. We have already emphasised that greater the acceleration of the reaction by the absorption of incident light, the less is the chance of observing a direct or a square relationship between intensity and velocity. Consequently Baly and Barker observed a ten-fold increase in intensity by increasing the light six-fold, whilst Mrs. Chapman working with a purer reacting system, containing less oxygen and under more intense light than that used by Baly and Barker observed about 5·5-fold increase of velocity on six-fold increase of light intensity. The results of Kornfeld and Müller are on the same line as those obtained by Mrs. Chapman.

Marshall working with very pure reacting substances and with intense light from a mercury arc obtained a relation, which is less than square-root for the same chemical change. Hence the photochemical combination of chlorine and hydrogen can show less than

square-root, direct or nearly square relationship depending on the acceleration caused by light. These results are exactly of the same type as those obtained by us with bromine and Rochelle salt, sodium formate and iodine, quinine sulphate and chromic acid and potassium oxalate and iodine.

Direct proportionality between intensity and velocity has been found in the cases of hydrolysis of chloroplatinic acids (Boll, *Ann. Phys.*, 1914, *ix*, **2**, 5, 226), the decompositions of solutions of hydrogen peroxide (Tian, *ibid*, 1916, *ix*, **5**, 248), potassium cobalti-oxalate (Vránek, *Z. Elektrochem.*, 1917, **23**, 336) and potassium mangani-oxalate (Ghosh and Kappanna, *J. Indian Chem. Soc.*, 1926, **3**, 127), and for the initial photolysis of uranyl formate solutions (Hatt, *Z. physikal. Chem.*, 1918, **92**, 513). Now in all these cases there is an appreciable dark reaction and in presence of light the velocity of the reaction is not enormously increased. Moreover Mukerji and Dhar (*loc. cit.*) found that a solution of dicyanin can be decolourised by passing oxygen in the dark and the effect of light intensity on the photochemical bleaching of dicyanin shows direct proportionality. On the other hand Warburg and Negelein (*Z. physikal. Chem.*, 1923, **106**, 191) have shown that in the carbon dioxide assimilation reaction sensitised by chlorophyll, the rate of assimilation increases less rapidly than the intensity. It is well known that no combination of carbon dioxide and moisture takes place in the dark even in presence of chlorophyll and hence carbon assimilation is a typically photochemical reaction where the velocity does not increase proportionately with the intensity of light. According to Berthoud (*Trans. Faraday Soc.*, 1925, **21**, 554 ; also Berthoud and Nicolet, *Helv. Chim. Acta*, 1927, **10**, 475) square root relationship holds for addition of bromine to cinnamic acid, to α-phenylcinnamonitrile and to stilbene and the oxidation of hydriodic acid in presence of iodine. In all these cases the reactions are highly accelerated by light and the reaction velocity in the dark is very small in comparison with the photochemical velocity.

Bodenstein and Lutkemeyer (*Z. physikal. Chem.*, 1924, **114**, 208) have announced that the union of hydrogen and bromine in light is proportional to the square-root of the energy absorbed when the intensity of light is kept constant. It will be interesting to observe that the velocity of the same reaction taking place in the light is 30 times greater than that taking place in the dark. Consequently the combination of bromine and hydrogen is highly photochemical

in nature. Briers and Chapman (*J. Chem. Soc.*, 1928, **133**, 1807) have recently found that the rate of interaction of hydrogen and bromine for very high intensity of light approximates to values which are square-root to the values of the intensity but for low intensities, the rate becomes more nearly equal to values proportional to intensity. Those reactions where square-root relationship is observed are largely accelerated by light and their thermal reactions are extremely slow in comparison with the reaction in light alone. In these reactions many molecules are readily activated by the absorption of radiation on illumination and consequently further increase in light intensity is not likely to increase the velocity of reaction markedly.

In previous papers (*J. Chem. Soc.*, 1917, **111**, 707; *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 308; *J. Phys. Chem.*, 1924, **28**, 948; *Z. anorg. Chem.*, 1924, **141**, 1; *Z. Elektrochem.*, 1925, **31**, 283) the conception of activation of molecules in explaining the mechanism of thermal and photochemical reactions has been emphasised. It has been postulated that chemical reactions take place between activated molecules. It has also been pointed out that the effects of increase of temperature, of light and of chemical catalysts in a reaction are intimately connected and are possibly identical in nature. It has also been shown that those reactions which are very sensitive to the influence of temperature are also very sensitive to the influence of light. Moreover, we have proved (*J. Chem. Soc.*, 1917, **111**, 707; 1923, **123**, 1856; *Z. anorg. Chem.*, 1922, **121**, 1561; 1924, **134**, 172; 1923, **169**, 381; 1920, **176**, 372) with numerous reactions that light acting as a positive catalyst markedly lower the temperature coefficient of a reaction; for, in presence of light the transformation from an inactive to active molecules would have already taken place and therefore, temperature should have less additional accelerating effect. Consequently those reactions which are highly photochemical in nature have much less chance of showing direct proportionality between the incident light and velocity of reaction.

A fast dark reaction when illuminated, has much less chance of showing direct proportionality relationship than a slow reaction, because in a fast reaction many more molecules are in the active state and there is less chance of further activation of molecules on increased illumination than in the case of slow reactions. As a matter of fact, our experimental results show that the reaction

between potassium permanganate and lactic acid, or tartaric acid or citric acid in presence of strong light increases much less rapidly than intensity and these reactions have been proved to be fast in the dark.

The majority of researchers in photochemistry have assumed that the amount of a chemical change in a given system, effected by light of a specified wave-length, is directly proportional to the light absorbed. Following the lead of Draper this has been called the first law of photochemistry. Although this is a fundamental principle of greatest importance, the experimental evidence of its universal validity is not conclusive. From a survey of our experimental results obtained with more than forty photochemical reactions and the existing literature in photochemistry, we come to the conclusion that the amount of chemical change of a truly photochemical system where the reaction is largely accelerated by light, is proportional to the square root or even less than square-root of the light absorbed.

In recent years Berthoud (*Helv. Chim. Acta*, 1924, **7**, 324) has emphasised that the primary process in the photochemical reactions with halogens as one of the reacting substances is the dissociation of halogen molecules into atoms as the result of their absorption of light, the halogen atoms then reacting at a rate proportional to the first power of their concentration. This contention of Berthoud appears to be supported by the fact that several photochemical reactions are proportional to the square-root of the incident radiation.

In foregoing papers (*J. Phys. Chem.*, 1928, **32**, 1308; *Z. anorg. Chem.*, 1928, **169**, 281; 1928, **175**, 257) we have shown that this point of view of Berthoud need not always be correct. We have observed that the reaction between potassium oxalate and iodine is proportional to the square-root of the incident radiation from a 1000 watt gas-filled tungsten filament lamp; whilst the reaction between sodium lactate and iodine is directly proportional to the intensity. If we assume that in presence of light a molecule of iodine is atomised, we can explain the intensity effect on the reaction between potassium oxalate and iodine, but this conception that the halogen molecules are atomised on illumination does not help us in understanding the mechanism of those photochemical reactions with halogen as one of the reacting substances and where the velocity of reaction is directly proportional or proportional to the square of the intensity of the incident radiation.

Our experimental results show that the reaction between sodium lactate and iodine is only slightly accelerated by light and consequently the inactive molecules available for activation on illumination is large and hence direct proportionality is observed. Moreover we have shown in this paper that in the case of several photochemical reactions, the relation between velocity and intensity of incident radiation changes from $\frac{1}{3}$ to 2. In other words, we have shown definitely that the ratio of the velocity and intensity of one and the same photochemical reaction can vary from a proper fraction to 2 or more depending on the acceleration of the photochemical reaction over the thermal reaction. We are of the opinion that this explanation of the difference of intensity effect on different photochemical reactions is more satisfactory than any of the existing views.

Baly and Barker and others have assumed that those reactions, which do not obey Einstein law of photochemical equivalence, should deviate from Draper's law. We have shown that the bleaching of neocyanin in air follows Einstein's law of photochemical equivalence but this reaction is proportional to the square-root of the incident radiation. Moreover, the reactions between iodine and a tartrate or lactate or citrate or ferrous sulphate and in several other cases the velocities are directly proportional to the intensity of incident radiation and hence follow Draper's law, although they deviate considerably from Einstein's law of photochemical equivalence ; in all these reactions many more molecules react per quantum of light absorbed.

Hence we are of the opinion that those reactions which obey Einstein's law need not follow Draper's law and *vice versa*.

Summary.

(1) The influence of the change of intensity on the velocity of a photochemical reaction has been investigated with 35 photochemical reactions in solution in these laboratories.

(2) The reaction between potassium oxalate and aqueous iodine tends to be directly proportional to the intensity of radiation of wave-lengths 5650 Å and 7304 Å. The same reaction in presence of potassium iodide when exposed to white light or light of wave-length 4725 Å is proportional to the square-root of the incident radiation.

(3) The reaction between sodium potassium tartrate and bromine appears to be proportional to the square-root of the incident radiation

from a 1000 watt lamp. In presence of radiation of wave-length 5650 Å, it is directly proportional to the incident radiation and in presence of borax it tends to be proportional to the square of the incident radiation.

(4) The reaction between quinine sulphate and chromic acid appears to be proportional to the square-root or direct or more than direct of the incident radiation as the concentration of sulphuric acid is increased.

(5) The reaction between sodium formate and iodine dissolved in small amount of potassium iodide and sodium acetate tends to be proportional to the incident radiation. In presence of borax the velocity of the same reaction becomes about nine-fold when the intensity is increased six times. In presence of excess of potassium iodide and borax it tends to be proportional to the square-root of the incident radiation.

(6) The photochemical reaction between hydrogen and chlorine becomes proportional to the square-root of the incident radiation in presence of strong light and directly proportional when the acceleration is not high. An explanation of the existing divergent data on the influence of radiation on this reaction has been advanced.

(7) The combination of bromine and hydrogen becomes proportional to the square root in strong light and directly proportional in light of low intensity.

(8) The two important factors which are of consequence in the relation between intensity and velocity of a photochemical reaction are (*a*) the amount of absorption of the incident radiation by the reacting system and (*b*) the acceleration of the reaction in presence of light.

(9) Truly photochemical reactions should tend to be proportional to the square-root or less than square-root of the incident radiation.

(10) Those photochemical reactions which obey Einstein's law of photochemical equivalence need not follow Draper's law and *vice versa*.

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On the Effect of Alkali on Oleate and Taurocholate Hemolysis.

By Kshitish Chandra Sen, Amaresh Chandra Roy and Narendra Nath Mitra.

In a previous paper in this *Journal* (Sen and Mitra, 1928, **5**, 683) it has been shown that alkali has a peculiar effect on oleate hemolysis. It was observed that under the conditions of the experiment, the presence of small amount of alkali accelerated the hemolysis by oleate when the latter was present in small amounts, but retarded the hemolysis when the latter was present in higher amounts, as compared to pure oleate hemolysis. This behaviour appeared to be a peculiar one and deserved to be further investigated ; and we have now come to the conclusion that the observed results given in our previous paper were only a part of a very interesting phenomenon. We have made also some further investigations on the effect of alkali on taurocholate hemolysis and the results will be given in the proper place. The experimental methods are the same as given in our previous papers, the solutions being all made in normal saline. The total volume in each experiment was 5 c.c. and a suspension of sheep corpuscles was used. In Table I, 1 c.c. of a 0·2% suspension was used, the concentration of oleate being 1 in 10,000 and of caustic soda being $N/100$.

Table I.*

Amount of oleate in c. c.	Time for hemolysis with oleate in presence of $N/100$-NaOH in c.c			
	0·0	0·1	0·2	
0·0	—	No hemolysis in 2 hrs.	No hemolysis in 2 hrs.	
0·1	20% hemolysis in 1½ hrs.	20% hemolysis in 1½ hrs.	—	
0·2	64 mins. 0 sec.	25% hemolysis in 1½ hrs.	No hemolysis in 25 mins.	
0·3	29 0	25% hemolysis in 1½ hrs.	—	
0·4	10 34	57 min. 0 sec.	Partial hemolysis in 25 mins.	
0·5	9 0	50% hemolysis in 1½ hrs.	—	
0·6	5 41	40% hemolysis in 2 mins.	70% hemolysis immediately.	
0·7	4 28	50% hemolysis in 2 ,,	—	
0·8	3 56	70% hemolysis in 2 ,,	80% hemolysis immediately.	
0·9	2 44	90% hemolysis immediately	—	
1·0	2 32	90% hemolysis immediately	0 min. 52 secs.	
1·2	2 2	0 min. 30 secs.	—	

* In this and some other tables, the results expressed as 80 or 90% hemolysis immediately, probably indicated a complete hemolysis of the corpuscles, but accurate determination of the end-point was interfered by the formation of 'ghosts' in the liquid.

TABLE II.

Concentration of corpuscles = 1%. Concentration of alkali = $N/25$.

Amount of oleate in c.c.	Time for hemolysis with oleate in presence of $N/25$-NaOH in c. c.		
	0·0	0·1	0·2
0·0	—	5% hemolysis in 4 hrs.	142 mins. 0 secs.
0·2	No hemolysis in 4 hrs.	194 mins. 0 sec.	80 0
0·3	,,	171 0	90 0
0·4	95% hemolysis in 4 hrs.	183 0	87 91
0·5	130 min. 0 secs.	203 0	88 43
0·8	18 ,, 24 ,,	—	71 10
1·0	15 ,, 0 ,,	115 0	45 0
1·2	13 ,, 2 ,,	—	0 34
1·5	11 ,, 24 ,,	1 14	0 36
2·0	8 ,, 9 ,,	0 24	Immediate hemolysis.

TABLE III.

Concentration of corpuscles = 5%. Concentration of alkali = $N/25$. Concentration of oleate = 1 in 5000.

Amount of oleate in c.c.	Time of hemolysis with oleate in presence of $N/25$-NaOH in c.c.		
	0·0	0·1	0·2
1·5	8 min. 27 secs.	30% hemolysis in 2½ hrs.	70% hemolysis in 2½ hrs.
2·0	4 12	,, ,,	3 mins. 12 secs.
2·5	3 51	24 mins. 26 secs.	2 ,, 0 ,,
3·0	2 43	70% hemolysis in 1 hr.	Immediate hemolysis.
3·5	1 40	,, ,,	Immediate hemolysis.

It will be observed from these tables that excepting some data in Table II, no accelerating action of small amounts of alkali with small amounts of oleate was observed as was found to be the case in our previous paper. An investigation carried out to determine the cause of this difference showed that this phenomenon was probably due to a difference in the temperature in which these two experiments were conducted. Since the present experiments have been carried on at a temperature of 24° and our previous experiments were carried out at a temperature of 32°, we decided to repeat our experiments at the higher temperature and the following table shows a set of results carried out at 32°.

TABLE IV.

Concentration of corpuscles = 5%. Concentration of alkali = $N/10$. Concentration of oleate = 1 in 10,000.

Amount of oleate in c.c.	Time of complete hemolysis with oleate in presence of $N/10$-NaOH in c.c.	
	0·0	0·1
0·0	—	No hemolysis in 4 hrs.
0·8	5% hemolysis in 3½ hrs.	145 mins. 12 secs.
1·0	30% ,,	170 ,, 0 ,,
1·2	118 mins. 0 sec.	175 ,, 0 ,,
1·4	81 ,, 0 ,,	60% hemolysis in 120 mins.

From the foregoing results, it will be observed that the effect of alkali is different with different concentrations of oleate. Thus when the oleate concentration is comparatively small, the hemolytic efficiency of the mixture of alkali and oleate may, under certain circumstances, become greater than that of pure oleate. With medium concentrations of oleate, however, a mixture of oleate and alkali has a markedly lower hemolytic power than the pure oleate. While again with comparatively higher concentrations of oleate, a mixture of alkali and oleate has a markedly greater hemolytic efficiency than the pure oleate itself. Hence when the alkali concentration is constant, we can get either an increase or a decrease of the hemolytic efficiency of a mixture of oleate and alkali depending on the particular concentration of the oleate used. The reason of this peculiar behaviour exhibited by alkali is however not very clear. Another interesting thing to be noticed in the foregoing results is that in the presence of alkali, the time-dilution curves of oleate hemolysis are not always of a simple nature but often show considerable abnormalities. We have repeated our experiments many times and have come to the conclusion that these abnormalities are not due to any experimental error ; but are due to some particular conditions such as concentration of the cells, temperature, etc., under which the experiments are made.

So long we have investigated the hemolytic effect of a mixture of alkali and oleate on blood corpuscles. In some previous papers we have shown that normal serum either inhibits or accelerates hemolysis by some chemical hemolytes according to whether it is added together with the hemolyte or after the addition of hemolyte to the cells. The time-interval after which the serum is added to

the hemolyte and corpuscle mixture was also found to be an important factor. Since traces of alkali have been found to have an inhibiting action when added together with another chemical hemolyte in certain concentrations, it was thought desirable to investigate whether alkali, if added to a mixture of hemolyte and corpuscle, could accelerate the hemolysis. This would be interesting because a close similarity in the actions of serum and alkali can be established. In the following table some data of the effect of alkali on oleate hemolysis under different conditions are given.

TABLE V.

Conc. of corpuscles = 0·2%. Concentration of oleate = 1 in 10,000. 0·1 C.c. *N*/100-NaOH added each time.

Amount of oleate in c.c.	Time of hemolysis with pure oleate.	Time of complete hemolysis when the alkali was added *x* minutes after the addition of oleate to the cells.		
		$x = \frac{1}{2}$ minute.	$x = 1$ minute.	$x = 2$ minutes.
0·2	23 min 22 secs.	5% hemolysis in 2 hrs.	—	—
0·4	6 8	84 min. 37 secs.	60 min. 0 secs.	2 min. 44 secs.
0·6	3 15	20 28	1 ,, 24 ,,	Immediate hemolysis.
0·8	2 28	2 47	Immediate hemolysis.	—
1·0	2 1	1 20	,, ,,	—

It will be observed from this table that the effect of alkali on oleate hemolysis is quite analogous to that exerted by serum. Since serum exerts this inhibitory or acceleratory effect on taurocholate hemolysis also, it was thought desirable to study the effect of alkali on taurocholate hemolysis at this place. In Table VI these data are shown.

TABLE VI.

Conc. of corpuscles = 1%. Taurocholate concentration = 1 in 1,000. 0·1 C.c. *N*/25-NaOH used each time.

Amount of taurocholate in c.c.	Time of hemolysis with pure taurocholate.	Time of hemolysis when a mixture of alkali and taurocholate was added to the cells.	Time of hemolysis when alkali was added 1 minute after the addition of taurocholate.
1·5	20 min. 5 secs.	55% hemolysis in 2 hours.	Immediate hemolysis,
2·0	12 42	70% ,, ,,	,, ,,
2·5	6 37	80% ,, ,,	,, ,,
3·0	4 50	120 min. 0 sec.	,, ,,

From the foregoing results of the effect of alkali on taurocholate and oleate hemolysis, it is apparent that alkali is behaving in an entirely similar way to that of serum so far as the inhibition or the acceleration of hymolysis is concerned. Since alkali has itself an hemolysing effect at higher concentrations, its action can be better compared to that of an hemolytic serum as studied in one of our previous papers. An important point in connection with this inhibitory or acceleratory effect of serums on taurocholate and oleate hemolysis arises here, namely, to what constituent of the serum is this particular behaviour due? Since normal serum is slightly alkaline, the presence of this alkali would no doubt have a marked action on the observed inhibition or acceleration of hemolysis. In one of our previous papers we have drawn attention of the early work of Sachs (*Biochem. Z.*, 1908, **12**, 278) who has shown that the serum proteins have some effect on this particular acceleration phenomenon. Without in any way committing ourselves to any particular hypothesis we may suggest that this acceleration of hemolysis by addition of normal serum may be, at least to a certain extent, due to the alkali content of the serum.

Summary.

(1) An experimental study has been made of the effect of alkali on oleate and taurocholate hemolysis.

(2) It has been observed that in presence of alkali the time-dilution curves of oleate hemolysis show some abnormalities in some cases.

(3) When traces of alkali are added to the cells together with the oleate, it may have either a retarding or an accelerating effect on hemolysis, as compared to pure oleate hemolysis, depending on the concentration of the oleate used. If the alkali is added to a mixture of oleate and corpuscles, a great acceleration of hemolysis can be easily obtained by suitably varying the amount of the oleate and the time-interval after which the alkali is added.

(4) A similar acceleration or retardation of taurocholate hemolysis can be observed in presence of traces of alkali depending on whether the alkali is added before or after the addition of the taurocholate to the cells.

(5) The alkali therefore behaves, in low concentrations, in a similar way as serum and it appears that the accelerating effect of normal serum on taurocholate and oleate hemolysis as studied in our previous papers, may, at least in part, be due to the alkali content of the serum.

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Benzidine Rearrangement in Heterocyclic Series. Part III.

By Bijoy Chandra Das-Gupta and Prafulla Kumar Bose.

In a recent communication, Bose and Sen (*J. Indian Chem. Soc.*, 1928, **5**, 643) showed that 1-*o*-tolyl- and 1-*m*-tolyl-thiosemicarbazides condense readily with halogenated ketones forming hydrazo-compounds which undergo benzidine rearrangement (*cf.* Bose, *J. Indian Chem. Soc.*, 1927, **4**, 331). 1-*p*-Tolylthiosemicarbazide, however, was found to behave in a different manner and formed imino-compounds. In the present investigation the action of the three nitrophenylthiosemicarbazides upon halogenated ketones has been studied.

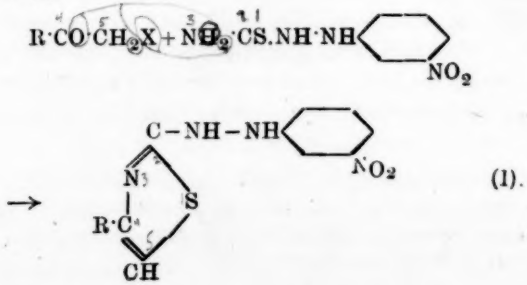
The reaction proceeded smoothly at the room temperature with the formation of products which could be divided into two classes:

(1) Those that behaved like hydrazobenzene towards hydrochloric acid, *e g.*, the products derived from 1-*m*-nitrophenylthiosemicarbazide.

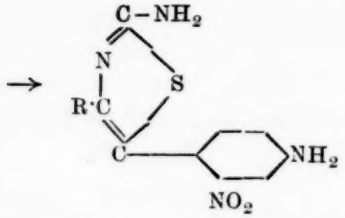
(2) Those that were unaffected by boiling hydrochloric acid but dissolved in aqueous ammonia or caustic alkalis with a deep violet colour. This group includes the products from the other two nitrophenylthiosemicarbazides.

In all the cases, the substances gave colour reactions with concentrated sulphuric acid and yielded monoacetyl derivatives on acetylation with acetic anhydride in presence of pyridine.

The course of the reaction may be represented as follows in the case of (1).



(1).

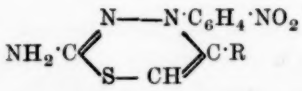


(II).

where X = halogen; R = CH_3, Ph or *p*-Tolyl.

The diamines thus obtained gave diacetyl derivatives on acetylation with acetic anhydride and formed dihydrochlorides and picrates. These bases dissolved in concentrated sulphuric acid without developing any colour.

The substances derived from the condensation of *o*-nitro- and *p*-nitro-phenylthiosemicarbazides with the halogenated ketones, as has been stated above, behaved differently. They did not undergo any change when boiled with hydrochloric acid of varying strengths in aqueous or in alcoholic solutions. Consequently, the hydrazo-structure (IV or VI) seems to be unacceptable for these compounds. Moroever, this fact is hardly in agreement with the expected behaviour of compounds having =NH or =N.NHR groups in the molecule.* The solubility of the compounds even in very dilute caustic alkalis and ammonia with the formation of deep violet colour followed by decomposition and separation of a black slimy precipitate, again, does not harmonise with the structure,



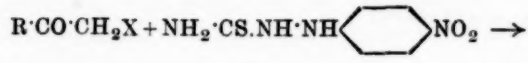
but recalls the behaviour of nitrophenylhydrazones † towards alkalis.

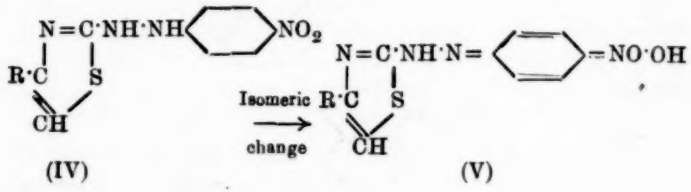
Chattaway and Clemo (*J. Chem. Soc.*, 1923, **123**, 3041; *cf.* also Hodgson and Beard, *J. Chem. Soc.*, 1927, **131**, 2375) made the interesting observation that many aldehyde-phenylhydrazones having one or more nitro-groups in the *ortho-* or *para-* (but not *meta-*) position to the aldehydo- or hydrazino-group dissolved in alkalis producing

* For the various possibilities of condensation, compare Bose (*loc. cit.*)

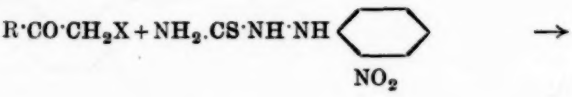
† *p*-Nitrophenylhydrazine itself was found to dissolve in aqueous alkali or ammonia forming a brownish violet solution, which decomposed on keeping. *m*-Nitrophenylhydrazine was unaffected in presence of alkali.

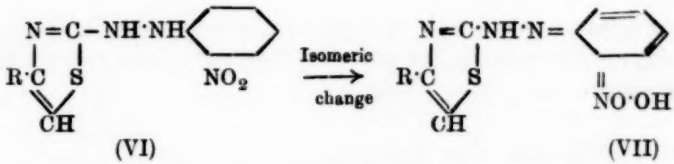
deep colours. They ascribed this remarkable property to a quinonoid configuration (*cf.* Lifschitz, *Ber.*, 1915, **48**, 1730 ; 1922, **55**, 1613) "although a quinonoid configuration is not a necessary condition of colour." Our observations with the products from the three nitrophenylthiosemicarbazides are capable of similar interpretation. The course of the reactions is indicated below:





(IV) (V)





(VI) (VII)

where X = halogen ; R = CH_3, Ph or *p*-Tolyl.

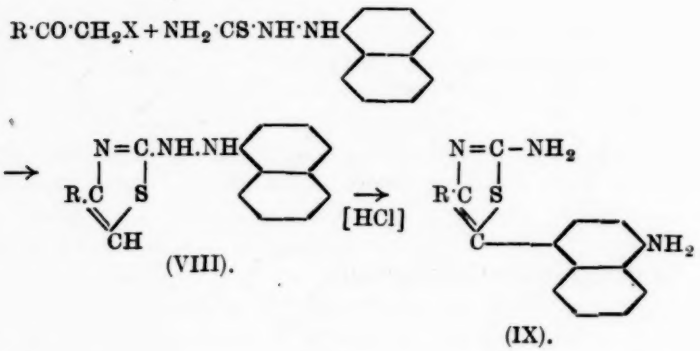
The formulæ (V) and (VII) harmonise with the observed properties of the compounds, namely—

(*a*) Solubility in aqueous alkalis with the formation of deep coloured solutions ; and

(*b*) Indifference towards hydrochloric acid.

The inability of the compounds under discussion to undergo benzidine transformation, however, does not at all affect our main issue, and we are of the opinion that benzidine transformation should occur in all compounds having the general formula RNH.NHR′, where R and R′ are either aromatic or heterocyclic nuclei provided the conditions laid down by Fargher and Pyman (*J. Chem. Soc.*, 1919, **115**, 225) be satisfied.

The case of α-naphthylhydrazinothiazoles, which were studied in this connexion, is also interesting from the point of view of the above statement. The compounds, which were prepared by condensing equimolecular quantities of 1-α-naphthylthiosemicarbazide and halogenated ketones at the ordinary temperature, shared all the properties of phenylhydrazinothiazoles described by Bose (*loc.cit.*) Obviously, the naphthalene-thiazole system comes under the generalisation proposed above.



Further investigations with symmetrically disubstituted hydrazines having pyridine, *iso*quinoline and other heterocyclic ring systems are in progress.

Experimental.

1-o-*Nitrophenylthiosemicarbazide*.—o-Nitrophenylhydrazine (15 g.) and potassium sulphocyanide (15 g.) were successively added to 60 c.c. of absolute alcohol containing dry hydrogen chloride gas (3·5 g.). The mixture was boiled on a water-bath under reflux for eight hours. The contents of the flask were then diluted with water (150 c.c.) and a little hydrochloric acid, and cooled when 1-o-nitrophenylthiosemicarbazide separated out (9 g.). It was crystallised from acetone in yellow plates, m.p. 201°. (Found: N, 26·12. $C_7H_8O_2N_4S$ requires N, 26·42 per cent.).

The method of preparation of the other thiosemicarbazides (*vide infra*) is essentially the same as described above.

1-o-*Nitrophenylthiosemicarbazide and ω-Bromoacetophenone: Formation of* VII (R=Ph).

1-*o*-Nitrophenylthiosemicarbazide (2 g.) was dissolved in alcohol (20 c.c.) and ω-bromoacetophenone (1·9 g.) was added gradually to the cold solution with constant shaking. The reaction was followed by development of heat and appearance of the condensation product. After a few minutes pyridine (4 c. c.) was added when the product dissolved. Water was then added to precipitate the base which was then collected and washed with water and dilute alcohol (yield almost quantitative). The substance was crystallised from acetone (charcoaled) in brown plates which decomposed at 190°. (Found: C, 57·63; H, 3·77; N, 18·12. $C_{15}H_{12}O_2N_4S$ requires C, 57·69 ; H, 3·85; N, 17·95 per cent.).

The substance is soluble in alcohol, acetone and pyridine. It gives a deep brown colour with concentrated sulphuric acid. It dissolves in caustic alkalis giving a deep violet solution. It remained unchanged even on prolonged boiling with hydrochloric acid.

The *monoacetyl* derivative, obtained in the usual manner, crystallised from acetone (charcoaled) in yellow needles, m. p. 175°. (Found: N, 15·96. $C_{17}H_{14}O_3N_4S$ requires N, 15·82 per cent.).

1-o-*Nitrophenylthiosemicarbazide and* p-*Methyl-ω-bromoacetophenone*: *Formation of* VII [R=$CH_3.C_6H_4$–(para)].

The procedure was similar to that described above (yield, 1·6 g. from 1·6 g. of 1-*o*-nitrophenylthiosemicarbazide). The product formed orange needles from acetone, m. p. 185° with decomp. (Found: N, 17·12. $C_{16}H_{14}O_2N_4S$ requires N, 17·18 per cent.). In properties and solubilities it resembled the phenyl compound described above.

The *monoacetyl* derivative crystallised from acetone in yellow plates, m. p. 206°. (Found: N, 15·16. $C_{18}H_{16}O_3N_4S$ requires N, 15·22 per cent.).

1-o-*Nitrophenylthiosemicarbazide and Monochloroacetone*: *Formation of* VII (R=CH_3).

The product, when prepared and purified as stated above, formed yellow plates (from acetone) which assumed a dark colour on standing. It decomposed at 165°. (Found: N, 22·16. $C_{10}H_{10}O_2N_4S$ requires N, 22·4 per cent.).

The substance gave a greenish-brown colour with concentrated sulphuric acid and a deep violet solution with caustic alkalis or ammonia.

The *monoacetyl* derivative separated from acetone in yellow needles, m. p. 167°. (Found: C, 48·9; H, 4·42; N, 19·39.

$C_{12}H_{12}O_3N_4S$ requires C, 49·32 ; H, 4·11; N, 19·18 per cent.).

1-m-*Nitrophenylthiosemicarbazide*.—From 17 g. of *m*-nitrophenylhydrazine, 10 g. of the product were obtained. It was crystallised from alcohol in orange-yellow aggregates, m. p. 187°. (Found: N, 26·62. $C_7H_8O_2N_4S$ requires N, 26·42 per cent.).

2-m-*Nitrophenylhydrazino*-4-*phenyl*-1:3-*thiazole* (*Formula* I, R=Ph).—1-*m*-Nitrophenylthiosemicarbazide (1·8 g.) was dissolved in absolute alcohol and ω-bromoacetophenone (1·7 g.) added at the ordinary temperature (25°). Subsequent procedure was as usual, the yield being 2·4 g. The base was crystallised from a mixture of pyridine and dilute alcohol in yellow, star-like crystals melting at 192–3°. (Found: N, 18·17. $C_{15}H_{12}O_2N_4S$ requires N, 17·95 per cent.).

It was soluble in acetone, alcohol, and pyridine and gave a deep reddish-brown colour with concentrated sulphuric acid. Caustic alkalis have no action upon it in the cold.

The *monoacetyl* derivative was crystallised from acetone in straw-yellow needles, m. p. 186°. (Found: N, 15·79. $C_{17}H_{14}O_2N_4S$ requires N, 15·82 per cent.).

2-*Amino*-4-*phenyl*-5-o-*nitro*-p-*aminophenyl*-1:3-*thiazole* (*Formula* II, R=Ph).—The hydrazinothiazole described above (1·5 g.) was boiled with 130 c.c. of hydrochloric acid (1:3) for 45 minutes until it had completely dissolved. The solution was then filtered and cooled. On neutralising the solution with concentrated ammonia, a precipitate (0·9 g.) was obtained. It was crystallised from alcohol (charcoaled) in reddish-orange needles, m.p. 253°. (Found: N, 17·97. $C_{15}H_{12}O_2N_4S$ requires N, 17·95 per cent.).

The base did not impart to sulphuric acid any colour. It formed a *picrate*, m.p. 213° (brown plates).

The *dihydrochloride* was obtained by dissolving the base in hot dilute hydrochloric acid. The solution was treated with animal charcoal and filtered hot. On adding concentrated hydrochloric acid and allowing to stand, the hydrochloride crystallised out in light yellow needles which decomposed at 230°. (Found: Cl, 18·02. $C_{15}H_{12}O_2N_4S$, 2HCl requires Cl, 18·42 per cent.).

The *diacetyl* derivative crytallised from acetone in orange plates, decomposing above 295°. (Found : N, 14·13. $C_{19}H_{16}O_4N_4S$ requires N, 14·14 per cent.).

2-m-*Nitrophenylhydrazino*-4-p-*tolyl*-1:3-*thiazole* (*Formula* I, R=*p*-Tolyl).—The condensation was carried out in acetone solution

using equimolecular quantities of 1-*m*-nitrophenylthiosemicarbazide and *p*-methyl-ω-bromoacetophenone. The product crystallised from acetone in buff-coloured needles, m.p. 189°. (Found: C, 59·22; H, 4·67; N, 17·19. $C_{16}H_{14}O_2N_4S$ requires C, 58·9; H, 4·29; N, 17·18 per cent.). It gave a deep brown colouration with sulphuric acid.

The *monoacetyl* derivative crystallised from dilute alcohol in colourless needles, m.p. 178°. (Found: N, 15·26. $C_{18}H_{16}O_3N_4S$ requires N, 15·20 per cent.).

2-*Amino*-4-p-*tolyl*-5-o-*nitro*-p-*aminophenyl*-1:3-*thiazole* (*Formula* II, R=*p*-Tolyl).—The hydrochloride of the base was found to be sparingly soluble even in boiling water. Hence the conversion was effected in alcoholic medium, the duration of heating under reflux being about two hours. The product crystallised from alcohol in deep brown plates, m. p. 163° with decomp. (Found: N, 17·37. $C_{16}H_{14}O_2N_4S$ repuires N, 17·18 per cent.).

The *diacetyl* derivative formed brownish needles (from alcohol) melting at 253° with decomposition. (Found: N, 13·65. $C_{20}H_{18}O_4N_4S$ requires N, 13·75 per cent.).

2-m-*Nitrophenylhydrazino*-4-*methyl*-1:3-*thiazole* (*Formula* I, R=CH_3).—Equimolecular quantities of monochloroacetone and 1-*m*-nitrophenylthiosemicarbazide were employed, as in the previous cases, the medium being alcohol. The base crystallised from acetone in dark plates decomposing at 138°. (Found: N, 22·38. $C_{10}H_{10}O_2N_4S$ requires N, 22·40 per cent.).

The base gave a greenish-brown colouration with concentrated sulphuric acid.

The *monoacetyl* derivative crystallised from acetone in orange crystals, m. p. 155°. (Found: N, 19·45. $C_{12}H_{12}O_3N_4S$ requires N, 19·18 per cent.).

2-*Amino*-4-*methyl*-5-o-*nitro*-p-*aminophenyl*-1:3-*thiazole* (*Formula* II, R=CH_3).—The thiazole described above (Formula I, R=CH_3) was boiled with 2*N*-hydrochloric acid. It readily dissolved forming an orange-red solution which turned yellow on further boiling. The filtered solution was cooled and treated with an excess of ammonia. The base was crystallised from a mixture of pyridine and dilute alcohol in deep brown needles, which decomposed at 110°. (Found: S, 12·93. $C_{10}H_{10}O_2N_4S$ requires S, 12·80 per cent.).

The *diacetyl* derivative formed yellow crystals (from methyl alcohol) decomposing at 180°. (Found: N, 17·12. $C_{14}H_{14}O_4N_4S$ requires N, 16·77 per cent.).

1-p-*Nitrophenylthiosemicarbazide*.—Of the three nitrophenylthiosemicarbazides, the yield, under identical conditions, was found to be greatest in the case of the *para*-compound, 15 g. of *p*-nitrophenylhydrazine giving 18 g. of the product. It was first crystallised from pyridine and finally from alcohol in yellow aggregates melting at 203°. (Found: S, 14·85. $C_7H_8O_2N_4S$ requires S, 15·09 per cent.).

1-p-*Nitrophenylthiosemicarbazide and ω-Bromoacetophenone: Formation of* V (R=Ph).—The usual method was followed. The product separated from acetone in shining, brown plates, m. p. 189° with decomp. (Found: C, 57·63; H, 3·91; N, 17·91. $C_{15}H_{12}O_2N_4S$ requires C, 57·69; H, 3·85; N, 17·95 per cent.).

It gave a deep brown colour with concentrated sulphuric acid and a deep violet colour with caustic soda solution.

The *monoacetyl* derivative crystallised from alcohol in shining, white plates, m.p. 185°. (Found: N, 15·87. $C_{17}H_{14}O_3N_4S$ requires N, 15·82 per cent.).

1-p-*Nitrophenylthiosemicarbazide and* p-*Methyl-ω-bromoacetophenone: Formation of* V (R=*p*-Tolyl).—The resulting product formed light brown plates from acetone, m.p 178°. (Found: N, 17·22. $C_{16}H_{14}O_2N_4S$ requires N, 17·18 per cent.).

This compound, like the phenyl derivative, imparted a deep brown colour to concentrated sulphuric acid and an intense violet colour to caustic alkalis.

The *monoacetyl* derivative crystallised from acetone in white needles, m.p. 182°. (Found: N, 15·26. $C_{18}H_{16}O_3N_4S$ requires N, 15·20 per cent.).

1-p-*Nitrophenylthiosemicarbazide and Monochloroacetone*: (*Formation of* V (R=CH_3).—The resulting product formed yellow aggregates, when crystallised from acetone. It decomposed at 145°. (Found: N, 22·17. $C_{10}H_{10}O_2N_4S$ requires N, 22·4 per cent.).

The substance imparted a greenish-yellow colour to concentrated sulphuric acid and a violet colour to aqueous alkali solutions.

The *monoacetyl* derivative crystallised from acetone in white needles, m.p. 178°. (Found: N, 19·09. $C_{12}H_{12}O_3N_4S$ requires N, 19·18 per cent.).

2-α-*Naphthylhydrazino-4-phenyl*-1:3-*thiazole* (*Formula* VIII, R=Ph).—Obtained in the usual way from 1-α-naphthylthiosemicarbazide and ω-bromoacetophenone, the base was found to be hardly

soluble in alcohol and acetone. It was crystallised from hot pyridine by the addition of alcohol in almost colourless plates, m.p. 174°. (Found: N, 13·35. $C_{19}H_{15}N_3S$ requires N, 13·25 per cent.).

It imparted a corn-flower blue colour to concentrated sulphuric acid.

The *monoacetyl* derivative separated from alcohol in colourless needles, m.p. 160-161°. (Found: N, 11·8. $C_{21}H_{17}ON_3S$ requires N, 11·7 per cent.).

2-*Amino*-4-*phenyl*-5-(4′-*amino*-)-*naphthyl*-1:3-*thiazole* (*Formula* IX, R=Ph).—The naphthyl compound described above (2 g.), concentrated hydrochloric acid (25 c.c.) and rectified spirit (60 c.c.) were boiled together for half an hour. The base was isolated by making the solution alkaline with ammonia (yield, 1·8 g.). It was finally crystallised from dilute alcohol in colourless needles, m.p. 236° with decomposition. (Found: C, 71·83; H, 4·79. $C_{19}H_{15}N_3S$ requires C, 71·93; H, 4·73 per cent.).

The substance gave no colouration with sulphuric acid.

It formed a *picrate*, crystallisable from alcohol in yellow plates, m.p. 193°.

The *dihydrochloride* was obtained by dissolving the base in alcohol and passing hydrochloric acid gas. It formed white needles, m.p. 245° with decomp. (Found: Cl, 17·95. $C_{19}H_{15}N_3S,2HCl$ requires Cl, 18·30 per cent.).

The *diacetyl* derivative was very soluble in ethyl alcohol, acetone, acetic acid, benzene and ether. It was crystallised from methyl alcohol in colourless aggregates, m.p. 248°. (Found: N, 10·62. $C_{23}H_{19}N_3SO_2$ requires N, 10·50 per cent.).

2-α *Naphthylhydrazino*-4-p-*tolyl*-1:3-*thiazole* (*Formula* VIII, R=*p*-Tolyl).—The product was scarcely soluble in alcohol and acetone. When crystallised from hot pyridine by the addition of alcohol, it formed brownish needles, m.p. 180°. (Found: C, 72·42; H, 5·30. $C_{20}H_{17}N_3S$ requires C, 72·51; H, 5·15 per cent.),

It gave a deep blue colour with concentrated sulphuric acid.

The *monoacetyl* derivative was crystallised from dilute alcohol in colourless needles, m.p. 161°. (Found: N, 11·27. $C_{22}H_{19}ON_3S$ requires N, 11·26 per cent.).

2-*Amino*-4-p-*tolyl*-5-(4′-*amino*-)-*naphthyl*-1:3-*thiazole* (*Formula* IX, R=*p*-Tolyl).—The resulting base, after the usual treatment with alkali, was crystallised in colourless needles from acetone, m.p.

280°. It gave no colouration with sulphuric acid. (Found: N, 12·39. $C_{20}H_{17}N_3S$ requires N, 12·38 per cent.).

The *diacetyl* derivative was crystallised from methyl alcohol; m p. 208°. (Found: N, 9·95. $C_{24}N_{21}O_2N_3S$ requires N, 10·12 per cent.).

2-α-*Naphthylhydrazino*-4-*methyl*-1:3-*thiazole* (*Formula* IX, R=CH_3).—Slow crystallisation of the product (from monochloroacetone and 1-α-naphthylthiosemicarbazide) from pyridine and dilute alcohol gave long fibrous needles, m. p. 188° with decomp. (Found: N, 16·03. $C_{14}H_{13}N_3S$ requires N, 16·28 per cent.).

It imparted a greenish-blue colour to concentrated sulphuric acid.

The *monoacetyl* compound was crystallised from methyl alcohol; m.p. 149-150°. (Found: N, 14·21. $C_{16}H_{15}ON_3S$ requires N, 14·14 per cent.).

2-*Amino*-4-*methyl*-5-(4′-*amino*-)-*naphthyl*-1:3-*thiazole* (*Formula* IX, R=CH_3).—The base was boiled for half an hour with hydrochloric acid (1:1). On adding ammonia to the filtered and cooled solution, a tarry mass was obtained which solidified on standing.

It was found to be extremely soluble in ethyl alcohol, acetone and methyl alcohol. From benzene it separated in brown crystals which decomposed at 110°. (Found: N, 16·42. $C_{14}H_{13}N_3S$ requires N, 16·28 per cent.).

The *diacetyl* derivative was crystallised from methyl alcohol. It decomposed at 260°. (Found: N, 12·31. $C_{18}H_{17}O_2N_3S$ requires N, 12·39 per cent.).

In conclusion, we offer our best thanks to Sir P. C. Rây for his keen interest during this investigation.

University College of Science and Technology, Calcutta.

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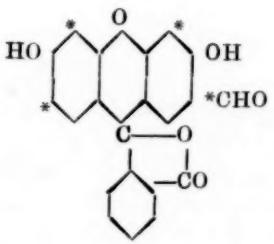
Aldehydofluorescein and Dyes Derived from it.

RAJENDRA NATH SEN AND KANAKENDRA NARAYON BANERJEA.

By the application of Reimer-Tiemann's reaction it has been found that the aldehyde group may be introduced into coumarin (Sen and Chakravarti, *J. Amer. Chem. Soc.*, 1928, **50**, 2428) or phenolphthalein (Sen and Kar, *J. Indian Chem. Soc.*, 1929, **6**, 54). Fluorescein also being subjected to the same reaction gives an aldehyde (I).



(I).

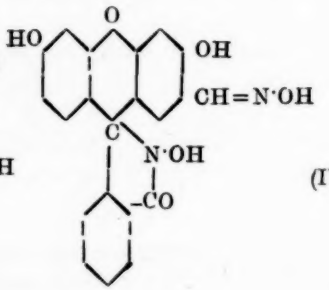
The aldehyde group may take any of the positions marked with asterisks, preferably a position *para* to the pyronine oxygen atom and *ortho* to any of the hydroxyl groups. The strength of the alkali to be used and the time and temperature of the reaction are of great importance to get a good yield of the aldehyde. After careful investigation, it has been observed that about 50% caustic soda solution and the temperature of the boiling water-bath for 15 to 20 hours give the best yield, which is about 45% of the theoretical. If alkali of lesser strength and lower temperature be used much unaltered fluorescein is left behind. The purification may be best effected through the bisulphite compound of the aldehyde as described in the experimental portion. It is really interesting to note that with the introduction of the aldehyde group in fluorescein, the fluorescence is diminished to a considerable extent. This diminution of fluorescent property may be ascribed to the fact that with

the introduction of the aldehyde group, the symmetry of the molecule is affected (Hewitt, *J. Chem. Soc.*, 1907, **91**, 1251). The aldehyde also differs from fluorescein in many other respects. Its solubility in absolute alcohol is much greater than that of fluorescein itself. In finely powdered state fluorescein exhibits a brick-red colour but the aldehyde in the same condition is yellowish brown. Whereas fluorescein gives a yellow solution with intense green fluorescence in alcohol, the aldehyde gives a deep red solution with much subdued green fluorescence in the same solvent. While fluorescein dyes wool and silk bright yellow shades, the aldehydofluorescein dyes wool and silk deep orange shades, the deeper colour being evidently due to the aldehyde group which acts as an additional chromophore. Fluorescein as well as the aldehyde are insoluble in water and also in ether, chloroform, benzene, etc., and both of them are soluble in alkali and also in alcohol and acetone.

The aldehyde gives a hydrazone (II), a semicarbazone (III), and a dioxime (IV).

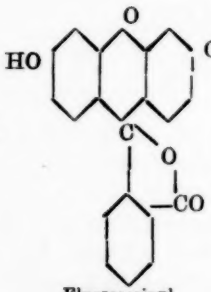
$R{\cdot}CH{=}N{\cdot}NHPh$ (II)

$R{\cdot}CH{=}N{\cdot}NH{\cdot}CO{\cdot}NH_2$ (III)



(IV).

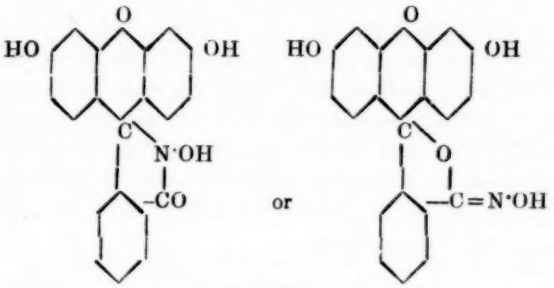
where R=



Fluoresceinyl.

It is noticed that the strong fluorescent property of fluorescein already diminished to a great extent by the advent of the aldehyde group disappears completely in hydrazone, semicarbazone and oxime. It appears that this may be due partly to the unsymmetry of the molecules and partly to the introduction of the nitrogen element in the molecules. It will be observed later on that with the introduction of the nitrogen atom in the molecule the fluorescent property generally disappears. The hydrazone, semicarbazone and dioxime all dye silk and wool dull pink shades.

The dioxime-formation is confirmed by the observation now made for the first time that fluorescein itself gives a monoxime (V) when treated with hydroxylamine hydrochloride under similar conditions (*cf.* phenolphthaleinoxime, *Ber.*, 1893, **26**, 172 ; *ibid*, 1895, **28**, 3258 ; Orndorff and Murray, *J. Amer. Chem. Soc.*, 19 7, **39**, 679).



(V)

Fluorescein itself is insoluble in ether, whereas its oxime is fairly soluble. It is very remarkable that the fluorescent property is not so markedly affected as in the case of the aldehyde and its hydrazone and oxime derivatives.

The aldehyde also gives a bisulphite compound which is very readily soluble in water and is not at all fluorescent even in alkaline solution.

Several interesting dyes with multiple chromophores have been derived from aldehydofluorescein. Thus (*i*) azomethine dyes have been obtained by condensing the aldehyde with monoamines, diamines and certain dyes containing free NH_2 groups ; (*ii*) triphenylmethane dyes have been obtained by condensing the aldehyde with dimethylaniline and *o*-cresotinic acid ; (*iii*) pyronine dyes have also been obtained by the condensation of the aldehyde with resorcinol and dimethyl-*m*-aminophenol.

To get azomethine dyes condensations have been effected in absolute alcoholic medium on the boiling water-bath. It is noted in this connection that alkaline solutions of these compounds do not exhibit any fluorescence. This is perhaps due to the entrance of the nitrogen element in the molecule. These compounds are generally coloured, micro-crystalline substances dyeing silk and wool with shades varying from yellow to reddish brown.

In cases of monoamines such as aminoazobenzene (VI), *p*-toluidine (VII) and *p*-nitraniline (VIII) only one molecule of the aldehyde reacts with one molecule of each of them.

$$R{\cdot}CH{=}N{\cdot}C_6H_4{\cdot}N{=}N{\cdot}Ph \qquad (VI)$$

$$R{\cdot}CH{=}N{\cdot}C_6H_4{\cdot}CH_3 \qquad (VII)$$

$$R{\cdot}CH{=}N{\cdot}C_6H_4{\cdot}NO_2 \qquad (VIII)$$

While the diamines such as benzidine (IX), *o*-phenylenediamine (X) and *p*-phenylenediamine (XI) react with two molecules of the aldehyde. *o*-Phenylenediamine and benzidine compounds dye silk and wool yellowish pink shades but the compound from *p*-phenylenediamine dyes silk and wool brown shades. All of them fail to exhibit any fluorescence in any solvent.

$$R{\cdot}CH{=}N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N{=}CH{\cdot}R \qquad (IX)$$

$$R{\cdot}CH{=}N{\cdot}C_6H_4{\cdot}N{=}CH{\cdot}R \qquad (X \text{ or } XI)$$

With *m*-phenylenediamine (XII), rosaniline (XIII) and chrysoidine (XIV) however, only one molecule of the aldehyde reacts, the presence of free amino-group being indicated by the evolution of nitrogen when heated with nitrous acid and also by the diazo-reaction and formation of azo-compounds. None of the products of these condensations exhibit any fluorescence in any solvent. Further, the intensity of colour of rosaniline and chrysoidine is also very much diminished by condensation with the aldehyde owing perhaps to the elimination of the auxochromic effect of one of the NH_2 groups.

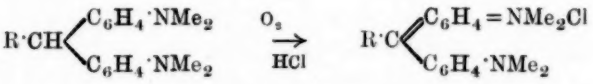
$$NH_2{\cdot}C_6H_4{\cdot}N{=}CHR \qquad (XII)$$

$$NH_2{\cdot}C_6H_4\diagdown\!\!\diagup C\diagup\!\!\diagdown OH \qquad (XIII)$$
$$NH_2{\cdot}C_6H_4\diagup\!\!\diagdown C_6H_4{\cdot}N{=}CH{\cdot}R$$

$$Ph{\cdot}N{=}N{-}$$
$$R{\cdot}CH{=}N{-}\text{(C}_6\text{H}_3\text{)}NH_2 \qquad (XIV)$$

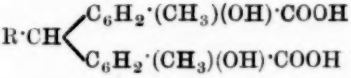
By the condensation of aldehydofluorescein with dimethylaniline, a leuco-base (XV) is obtained in colourless needle-shaped crystals which gradually turn bluish due to atmospheric oxidation, and gives

a beautiful blue basic dye when oxidized with lead peroxide in the usual manner. Unlike fluorescein and the aldehydofluorescein, the leuco-base is very readily soluble in cold chloroform giving a bluish-violet solution. It also differs from the aldehyde very markedly in other respects, *e.g.*, it is readily soluble in dilute hydrochloric acid giving a bluish-green solution and it is soluble in alcohol giving a violet solution but it is not soluble in caustic alkalis. In this case also it is noticed that the fluorescent property altogether disappears. Two molecules of dimethylaniline react with one molecule of the aldehyde. The hydrochloride (XVI) of the product derived from the leuco-base, on oxidation with lead peroxide in the usual manner, dyes wool and silk beautiful deep blue shades.



(XV) (XVI)

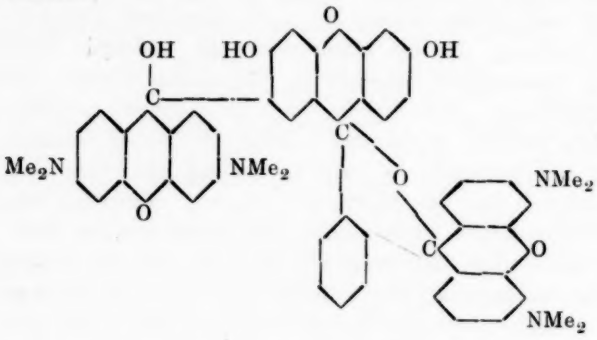
By the condensation of aldehydofluorescein with *o*-cresotinic acid in presence of sulphuric acid (*d* 1·84) in the cold, another triphenylmethane dye (XVII) has been obtained. The leuco-compound dyes silk and wool an orange-yellow shade which is deeper (*i.e.*, redder) than that of fluorescein itself and lighter (*i.e.*, more yellow) than that of the aldehyde. It is interesting to note that the compound exhibits fluorescence in alcoholic and alkaline solutions, which is more marked than that of aldehydofluorescein. Oxidation of the leuco-compound with nitrosyl sulphate gives a dark red compound which dyes silk and wool deep brown shades.



(XVII)

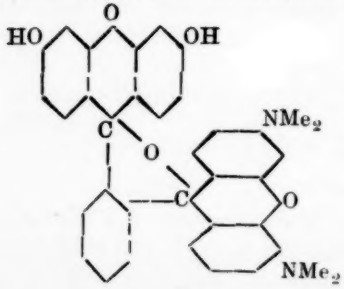
With dimethyl-*m*-aminophenol in the presence of sulphuric acid (*d* 1·84) at 160-170°, aldehydofluorescein gives a fine reddish-violet dye (XVIII) analogous to the rhodamines. Sulphuric acid in this case acts both as a condensing and an oxidizing agent, as is evidenced

by the copious evolution of sulphur dioxide during the course of the reaction.

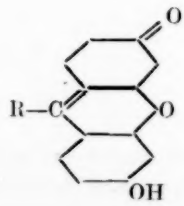


(XVIII)

It is to be noted however that below 140° there is practically no evolution of sulphur dioxide. Analytical results show that four molecules of dimethyl-*m*-aminophenol react with one molecule of aldehydofluorescein, both the CH:O and C:O groups taking part in the reaction. Sen and Guha-Sarkar studied the reactivity of the C:O group in the lactone ring (*J. Indian Chem. Soc.*, 1924, **1**, 150) and as further corroboration it is now found that fluorescein itself also condenses with two molecules of dimethyl-*m*-aminophenol in the presence of sulphuric acid (*d* 1·84) at 150-160° to give a compound (XIX) of the type of rhodamine which dyes silk and wool bluish-pink shades while the compound (XVIII) with the aldehyde dyes silk and wool a bluish-violet shade. It is interesting to note that both the compounds are strongly fluorescent in alcoholic and alkaline solutions. This may perhaps be due to the introduction of additional pyronine rings. Both the compounds are soluble in acid and alkali.



(XIX)



(XX)

Aldehydofluorescein has also been condensed with resorcinol (XX) in presence of sulphuric acid (*d* 1·84) at 100° for 3 to 4 hours in the manner described by Sen and Sinha (*J. Amer. Chem. Soc.*, 1923, **45**, 2984). Here two molecules of resorcinol react with one molecule of aldehydofluorescein giving a brownish red compound which dyes silk and wool red-orange shades. On brominating the compound, a deep red pentabromo-derivative is obtained which dyes silk and wool dark red shades. The compcund with resorcinol is more strongly fluorescent than the aldehyde and this may be ascribed also to the introduction of the additional pyronine ring.

Experimental.

Preparation of Aldehydofluorescein (I).—The crude aldehyde, prepared by the method applied in the case of aldehydophenolphthalein (Sen and Kar, *J. Indian Chem. Soc.*, 1929, **6**, 56) is extracted with cold absolute alcohol, the alcoholic extract poured into acidified water with constant stirring, the precipitate filtered, washed with warm water and finally crystallised from dilute alcohol. Yield 45%.

It may be obtained in an extra pure condition by decomposing, with hot dilute hydrochloric acid, the bisulphite compound of the aldehyde prepared by shaking, for a long time, a saturated aqueous solution of sodium bisulphite with the solid aldehyde which ultimately goes into solution. The bisulphite compound may also be obtained in light orange-yellow crystalline form by adding a saturated aqueous solution of sodium bisulphite to an absolute alcoholic solution of the aldehyde and keeping the mixture overnight. It is extremely soluble in cold water giving a light orange solution, and in alkali giving a deep red solution. It is insoluble in alcohol, chloroform, ether but soluble in acetone. It does not exhibit any fluorescence.

The aldehyde is a yellowish-brown micro-crystalline solid readily soluble in alkali, giving a dark red solution with green fluorescence. It is also soluble in alcohol, acetone, glacial acetic acid, nitrobenzene, but practically insoluble in ether, chloroform and benzene. It dyes wool and silk a bright orange shade. It does not melt up to 260°. (Found: C, 69·8; H, 3·7. $C_{21}H_{12}O_6$ requires C, 70·0; H, 3·3 per cent.)

Derivatives of Aldehydofluorescein.—The *phenylhydrazone* (II) was prepared by heating a mixture of the aldehyde and phenylhydrazine

in absolute alcohol on a water-bath for 2 to 3 hours ; on cooling, the hydrazone separated out. It was filtered, washed with acidified water and finally crystallised from dilute alcohol. It is a micro-crystalline powder, soluble in alcohol and acetone, and also in alkali with a deep red solution but no fluorescence. It does not melt up to 260°. (Found: N, 6·57. $C_{27}H_{18}O_5N_2$ requires N, 6·22 per cent.)

The *semicarbazone* (III) was prepared in the usual manner, and was crystallised from dilute alcohol ; a reddish-brown micro-crystalline substance, soluble in alkali, alcohol and acetone and insoluble in chloroform and ether was obtained. It does not melt up to 260°. (Found: N, 10·6. $C_{22}H_{15}O_6N_3$ requires N, 10·07 per cent.).

The *dioxime* (IV) was prepared as the dioxime of phenolphthalein-aldehyde (Sen and Kar, *loc. cit.*). The product when washed with acetone formed a dark red micro-crystalline powder, soluble in boiling water, alkali, dilute alcohol, and insoluble in chloroform, acetone, benzene and ether ; it does not melt up to 260°. (Found: N, 7·38. $C_{22}H_{14}O_6N_2$ requires N, 6·96 per cent.).

Fluorescein-monoxime (V).—Prepared and purified as the above dioxime ; it was finally extracted with ether. An orange-yellow micro-crystalline solid, soluble in alkali and alcohol with green fluorescence. It does not melt up to 260°. (Found: N, 3·6. $C_{20}H_{13}O_5N$ requires N, 3·7 per cent.).

Azomethine Dyes.

Fluoresceinal-aminoazobenzene (VI).— It was prepared as phenolphthaleinal-*p*-toluidine (*J. Indian Chem. Soc.*, 1929, **6**, 57), the heating being continued for 3-4 hours. The product is filtered, the residue washed with water acidified with hydrochloric acid, and finally with warm alcohol; crystallised from a mixture of alcohol and glacial acetic acid (4 : 1) as a reddish-brown micro-crystalline solid, soluble readily in glacial acetic acid and sparingly in alcohol and acetone. It does not melt up to 260°. It is not fluorescent, dyes yellow shade on wool and silk. Yield almost theoretical. (Found: N, 7·39. $C_{34}H_{21}O_5N_3$ requires N, 7·62 per cent.).

Other azomethine dyes are listed in the annexed table.

Triphenylmethane Dyes.

Tetramethyldiaminodiphenylfluorescein-methane (XV), prepared as the analogous compound of aldehydophenolphthalein (*J. Indian Chem. Soc.*, 1929, **6**, 58), crystallised from chloroform as light blue

small needles melting at 70°-72°. It is very readily soluble in chloroform, alcohol and ether giving reddish-violet solutions with no fluorescence. The acid solution is light bluish-green. Yield, 80 per cent. (Found: N, 5·05. $C_{38}H_{32}O_5N_2$ requires N, 4·79 per cent.).

The oxidation of the above leuco-base is carried out in the usual manner with freshly precipitated lead peroxide ; a bluish substance was obtained. The hydrochloride of this dyes a deep blue shade on wool and silk.

Dimethyldihydroxydicarboxydiphenylfluorescein-methane (XVII). —It was prepared as the analogous compound of aldehydophenolphthalein (*J. Indian Chem. Soc.*, 1929, **6**, 58). The product was washed with chloroform and crystallised from dilute alcohol as a micro-crystalline yellow substance, sparingly soluble in warm water, readily soluble in alcohol and acetone. Alkaline and alcoholic solutions exhibit red-green fluorescence ; it does not melt up to 260°. Light orange-yellow shade on silk and wool (yield, 80 per cent.). (Found: C, 68·2 ; H, 4·1. $C_{37}H_{26}O_{11}$ requires C, 68·7 ; H, 4·02 per cent.).

The above leuco-base is oxidised with nitrosyl sulphate at 50°-60° when a dark red powder soluble in alcohol and acetone is obtained. It dyes silk and wool a deep brown shade.

Pyronine Dyes.

Fluoresceinal-rhodamine (XVIII).—A mixture of dried aldehydofluorescein (2 g.), dried dimethyl-*m*-aminophenol (3 g.) and sulphuric acid (5 c.c., *d* 1·84) is heated on the oil-bath at 150°-160° for 4 to 5 hours with an air condenser. During the course of heating, sulphur dioxide is evolved as is evidenced by its odour and by the development of a blue colour on starch iodate paper. The molten mass is then cooled and treated with water, filtered and thoroughly washed with water. It is then dissolved in warm dilute hydrochloric acid and precipitated by ammonia. The solution and precipitation are repeated, and the washed residue is finally purified from alcohol and carbon bisulphide and obtained in the form of a pink powder. Yield, 70 per cent.

It dissolves in acid and alkalis with green-red fluorescence which is more marked in organic solvents ; it dyes wool and silk a fine bluish-violet shade. It does not melt up to 260°. (Found: N, 7·06. $C_{53}H_{48}O_7N_4$ requires N, 6·7 per cent.). Fluorescein itself condenses with dimethyl-*m*-aminophenol under similar conditions as above

and gives a reddish-pink substance, soluble in acids and alkalis and also in alcohol and acetone with marked green fluorescence. It dyes wool and silk a bluish pink shade. It softens at 245°. (Found: N, 4·96. $C_{36}H_{30}O_5N_2$ requires N, 4·91 per cent.).

Diresorcinol-fluoresceinein.— A mixture of aldehydofluorescein (2 g.), dried resorcinol (4 g.) and sulphuric acid (3 c.c., *d* 1·84) is heated on the boiling water-bath for 2 hours with an air condenser. Copious evolution of sulphur dioxide takes place. The melt, when cooled, is treated with ice-cold water, filtered and thoroughly washed with cold water. The residue is dissolved in caustic soda solution, and the compound is precipitated with dilute hydrochloric acid: the solution and precipitation are repeated several times. The product is then dissolved in alcohol and boiled with animal charcoal several times. The cooled filtrate is poured into water till a turbidity is produced. It is then filtered and the filtrate allowed to stand overnight with more water. The precipitate, thus obtained, is filtered and dried on a porous plate and finally in a desiccator (yield, 40 per cent.).

It is a dark red powder, sparingly soluble in cold water, easily soluble in alcohol and acetone, and insoluble in chloroform and ether. It imparts a red-green fluorescence, more intense than that of aldehydofluorescein, to alkaline and alcoholic solutions; it dyes wool and silk a red-orange shade; it does not melt up to 260°. (Found: C, 72·2; H, 3·75. $C_{33}H_{18}O_8$ requires C, 73·06; H, 3·3 per cent.).

The *pentabromo*-derivative was prepared and purified in the usual way. It is a deep red substance, insoluble in water, readily soluble in alkali and alcohol. It does not exhibit any fluorescence. It produces a deep red shade on silk and wool. (Found: Br, 42·01. $C_{33}H_{13}O_8Br_5$ requires Br, 42·6 per cent.).

Azomethine Dyes.

Name.	Formula.	Method of preparation.	M.P. and appearance.	P.c. of N (calc. values in brackets).	Properties.
Fluoresceinal-*p*-toluidine.	VII.	Aldehydofluorescein + *p*-toluidine (in alcohol) on water-bath for 3-4 hours. Yield, 90%.	Does not melt up to 260°. Reddish-brown powder.	3·08% (3·11)	Soluble in alkali giving red solution; sparingly soluble in alcohol; no fluorescence. Light yellow-orange shade on wool and silk.
-*p*-nitraniline.	VIII.	Aldehydofluorescein + *p*-nitraniline (in alcohol) on water-bath for 3-4 hours.	Does not melt up to 260°. Yellow powder.	5·6% (5·69)	Sparingly soluble in alcohol, insoluble in water and ether. Yellow shade on wool and silk.
-benzidine.	IX.	Aldehydofluorescein + benzidine (in alcohol) on water-bath for 3-4 hours. Yield, theoretical.	Does not melt up to 260°. Reddish-brown micro-crystalline powder.	3·57% (3·22)	Soluble in alkali giving a deep red solution, insoluble in water, boiling alcohol, chloroform and ether. No fluorescence.
-*o*-phenylenediamine.	X.	Aldehydofluorescein + *o*-phenylenediamine (in alcohol) on water-bath for 3-4 hours. Yield, 60%.	Does not melt up to 250°. Yellow powder.	3·69% (3·53)	No fluorescence. Sparingly soluble in alcohol and acetone, insoluble in water, ether and chloroform, Orange-yellow shade on wool and silk.
-*p*-phenylenediamine.	XI.	Aldehydofluorescein + *p*-phenylenediamine (in alcohol) on water-bath for 3-4 hours. Yield 40%.	Does not melt up to 260°. Yellowish-brown powder.	3·8% (3·53)	Very sparingly soluble in absolute alcohol; insoluble in water, ether and chloroform. No fluorescence. Brown shade on wool and silk.

Name.	Formula.	Method of preparation.	M.P. and appearance.	P.c. of N (calc. values in brackets.)	Properties.
-*m*-phenylene-diamine.	XII.	Aldehydofluorescein + *m*-phenylene-diamine (in alcohol) on water-bath for 3-4 hours. Yield, theoretical.	Does not melt up to 260°. Brown micro-crystalline powder.	6·23% (6·22)	Very sparingly soluble in cold alcohol, insoluble in water, ether and chloroform. Reddish-yellow shade on wool and silk.
Fluoresceinale-rosaniline.	XIII.	Aldehydofluorescein + rosaniline (in alcohol) on water-bath for 3-4 hours. Yield, theoretical.	Does not melt up to 260°. Reddish-violet powder.	6·3% (6·35)	Soluble in alkali giving a deep red solution with no fluorescence; sparingly soluble in alcohol, acetone and nitrobenzene; insoluble in water, ether, benzene and carbon tetrachloride. Pink shade on wool and silk.

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Chemical Examination of the Roots and Leaves of *Saussurea Lappa*, Clarke. Part I.

By Sudhamoy Ghosh, Nihar Ranjan Chatterjee and Ashutosh Dutta.

In a recent paper on the treatment of asthma with *Saussurea appa*, Chopra (*Indian Med. Gazette*, 1928, **63**, April issue), gives the following short but very useful summary of the plant and its uses: "This plant belongs to the natural order *Compositae*, and is commonly called *Kuth* or *Patchak* in Hindi, *Kustha* or *Kashmirja* in Sanskrit and *Kust* in Arabic and Persian. It was for a long time confused with other species of costus and also with orris root but Guibourt first suggested the correct botanical source of this drug and his suggestion was confirmed by the researches of Falconer who visited Kashmir and found that *Aplotaxis lappa* growing there was undoubtedly *Auclandia costus*, now known as *Saussurea lappa*. It is a tall, very stout herb, with annual stem, heart-shaped leaves and thick perennial roots which are dug up in the months of September and October. It grows chiefly on the moist and open slopes of the Himalayas, especially those surrounding the valley of Kashmir and adjacent ranges, at a height of 2,000 to 13,000 feet above sea level. The best root is grown over an altitude of 9,000 to 13,000 feet. The root occur in crooked twisted pieces about 3 inches long, ½ to 1 inch in diameter and possesses a pungent aromatic odour like that of orris root; it is collected and exported to China in large quantities without any further preparation. It is also shipped to the Red Sea and Persian Gulf. The root fetches a very good price, as much as Rs. 385 (£28-10) being at present paid for a maund (80 lb.) of a good sample in Calcutta. In China it is chiefly used as an incense, as a spice and medicinally as a powerful aromatic stimulant, carminative, antispasmodic and in the form of an ointment for external application. It is a very old remedy of the Hindu medicine and has been described in the Nighantas as a remedy for cough, asthma, fever, dyspepsia and skin diseases. The Arabian medical writers describe it as a diuretic and anthelmintic and use it in the treatment of quartan fever and leprosy."

In a previous paper, Chopra and De (*Indian Med. Gazette*, 1924, **59**, 540) gave an account of the antispasmodic action of the root in the treatment of bronchial asthma and, in the more recent paper referred to, Chopra has shown the remarkable effect of the drug in controlling the paroxysms of bronchial asthma.

In another paper recently communicated (*Indian J. Med. Res.*) Chopra and De have given a detailed description of the pharmacological action of the essential oil and the alkaloid (first isolated by us) which may be considered as the active principles chiefly responsible for the action of the drug in asthma. A summary of this is given later on.

Chemical Examination of the Root.

Of the active priciples contained in the root, only the essential oil was thoroughly examined by Semmler and Feldstein (*Ber.*, 1914, **47**, 2433). According to these workers, the essential oil has the following approximate composition. Camphene 0·04%; phellandrene 0·4%; terpene alcohol 0·2%; α-costene 6·0%; β-costene 6·0%; aplotaxene 20·0%; costol 7·0%; dihydrocostus lactone 15·0%; costus lactone 11·0%; costic acid 14·0%. The yield of the essential oil is stated to be about 1%.

No systematic study seems, however, to have been made for the other constituents. Hooper ("Pharmacographica Indica," 1890, Vol. II, p. 293) describes the presence of one solid and two liquid resins but he did not estimate their amount. He also mentions that he got evidence of the mere presence of an alkaloid, but he never isolated it. The isolation of the alkaloid was found by us to be a very difficult task and it took a long time to find out the proper technique for its purification.

The material employed in the present investigation was the genuine dry root supplied by the Kashmere State authorities, and we are grateful to them for this kind help.

For a systematic investigation, 500 gm. of the powdered root were extracted with petroleum ether (b. p. about 40°) for several days until exhausted. The extractive matter, freed from solvent, amounted to 6·4%. The extract, dissolved in petroleum ether, was shaken up repeatedly with water. The aqueous extracts, which had a bitter taste, were concentrated in *vacuo* and extracted in acid solution with ether. The small amount of bitter substance thus isolated was

amorphous and of non-alkaloidal nature. After extracting with water, the petroleum ether was removed and the residue was found to consist of an essential oil, some fixed oil and a little resin. The essential oil was separated by distillation in steam.

Ethereal Extract.—The roots, after extraction with petroleum ether, were extracted with ether until exhausted. The extract, which amounted to about 1·3%, gave tests for traces of tannins, a trace of the alkaloid and some of the bitter substances isolated above.

Absolute Alcoholic Extract.—After exhaustion with ether, the roots were exhausted with absolute alcohol, and the alcoholic extract amounted to about 11·8%. The residue, freed from alcohol, was taken up with water and the aqueous extract was shaken in slightly acid solution with ether. The residue from ethereal extract gave colour reactions for tannins. The aqueous solution was then made alkaline with ammonia and shaken repeatedly with ether and finally with chloroform. The ether extracted most of the alkaloid present.

The aqueous solution was next neutralised and precipitated with neutral lead acetate. The precipitate was washed, suspended in water and decomposed by sulphuretted hydrogen. The filtrate, after removal of lead sulphide, gave strong reactions for tannins, but nothing crystalline could be isolated. The filtrate from lead acetate precipitate was next precipitated by basic lead acetate. The precipitate was decomposed as before but nothing definite could be isolated. The filtrate from basic lead acetate was freed from lead and then evaporated in *vacuo*. Some of the bitter substance was isolated by chloroform, but nothing else of interest was obtained.

Aqueous Extract.—The roots, exhausted with alcohol, were then repeatedly extracted with hot water. On concentrating the aqueous extract in *vacuo*, a large amount of a white amorphous substance separated, which was purified and identified as inulin as described later. The yield of crude inulin amounted to nearly 18%. Some potassium nitrate and sugars were also detected in the aqueous extract.

Estimation of Essential Oil.—A weighed quantity of the powdered root was distilled in steam as long as the distillate was turbid. The distillate was then extracted with ether, the ethereal solution dried and ether removed. The average of two quantitative experiments gave 1·51% of essential oil for the sample examined. Previous experience showed that the yield of essential oil varied a good deal with different samples and was decreased by storage.

Resin.—A rough quantitative estimation of the amount of resin was carried out and the average of two estimations gave the value 6·0%.

Alkaloid (Assay).—The total alkaloidal content of a fresh sample as obtained by a general gravimetric method was found to be 0·052% as the average of 3 estimations. The amount of alkaloid varied in different samples and in one case it was extremely small.

Isolation of the Alkaloid.—About 1500 gm. of the powdered roots were extracted in the cold in a glass percolator with rectified spirit containing about 5% of ammonia until the alkaloid was all exhausted. The alcohol was recovered and the residue treated repeatedly with 1% sulphuric acid. The acid extract was made slightly alkaline with ammonia and shaken with chloroform. The chloroform was removed and the residue (still admixed with resinous matter) was dissolved in a little alcohol and neutralised with a little excess of tartaric acid. Water was added and the alcohol removed on the water-bath. The clear, pale yellow supernatant liquid was decanted off and concentrated on the water-bath until crystals were obtained. The highly coloured crystals were then dissolved in alcohol and precipitated by ether. The crystals were then washed several times with absolute alcohol to remove the excess of tartaric acid, resinous and colouring matters. They were next dissolved in a small quantity of hot water and decolourised with animal charcoal, filtered, and evaporated to crystallisation. The crystals were washed with absolute alcohol and then with ether and dried. They were perfectly colourless, needle-shaped crystals. Further chemical work with this new active alkaloid is in progress, and we have provisionally designated it as "Saussurine".

Inulin.—The crude inulin obtained before was dissolved in hot water, heated with animal charcoal and filtered hot. The precipitate obtained on cooling was dissolved in a small amount of hot water and precipitated by alcohol. On repeating the process, the substance was obtained as a perfectly white, amorphous powder without any taste. The air-dried sample melted at about 180° with decomposition and the melting point rose higher on prolonged drying in air oven. The substance was slightly soluble in cold water but dissolved easily in hot. It was insoluble in absolute alcohol, ether and benzene, but fairly soluble in dilute alcohol.

In aqueous solution the specific rotation, $[\alpha]_D^{25^\circ}$ was $-34{\cdot}0^\circ$. (The values for inulin given by different authors vary from -34° to -42°).

The estimations of C and H, the determination of the acetyl groups in the acetylated product, the osazone of the sugar obtained by its hydrolysis all confirmed the substance being a variety of inulin.

The large content of inulin in the roots can serve as an economic source of its manufacture. After the preparation of the liquid extract (see below), the residue (which is at present thrown away) can be utilised for its manufacture and will prove a useful by-product.

Examination of the Leaves.—The leaves were examined specially for essential oils and alkaloids. No essential oil could be obtained from the air-dry leaves supplied for examination. The alkaloidal content amounted to about 0·02% of the weight of the dry leaves. The nature of the alkaloid was the same as that found in the roots. It is, however, interesting to record that the alkaloid can be extracted much more easily from the leaves than from the roots owing to the absence of resinous and other matter present in the latter. And as the nature of the alkaloid is the same, the leaves, which are at present thrown away, may be utilised for the preparation of the pharmacologically active alkaloid.

" *Liquid Extract of Kut* ".—The liquid extract used for clinical trials is made by extracting the powdered roots repeatedly with 95% alcohol in the cold, and the solution is concentrated carefully until 1 c.c. of it corresponds to 1 g. of the root.

Pharmacological and Therapeutic Action.—The essential oil has antiseptic and disinfectant properties; it relaxes the involuntary muscle tissue; it is a cardiac stimulant, a carminative, an expectorant and a diuretic. The alkaloid, saussurine, has a depressant action on the vagus centre in the medulla as well as on the involuntary muscle fibres of the bronchioles and gastro-intestinal tract. It produces a slight but persistent rise of blood pressure and increases the force of contraction and amplitude of the ventricles.

The drug has a remarkable effect in controlling attacks of bronchial asthma especially those of the vagotonic type. The

paroxysms are cut short by the combined action of the essential oil and the alkaloid present in the root. The essential oil during its excretion in the lungs not only relaxes the bronchial muscle but has a marked expectorant action which relieves turgescence of the mucosa.

The drug is also useful in persistent hiccough.

Summary.

I. Constituents isolated in roots: –

Essential oil	...	... 1·5%
Resin	...	about 6%
Alkaloid (saussurine)		... 0·05%
Inulin	...	... 18%

A very small amount of a bitter substance.

Tannins in small amount.

Fixed oil, KNO_3, sugars, etc.

II. Constituent isolated in leaves: —

Alkaloid	... 0·02%

In conclusion, we desire to express our indebtedness to Col. R. N. Chopra and Capt. P. De for the study of the pharmacological and therapeutic properties of the drug.

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Relation between the Intensity and the Velocity of the Reaction between Potassium Oxalate and Bromine in Visible and Infra-red Radiations.

By A. K. Bhattacharya and N. R. Dhar.

In a recent communication (*J. Indian Chem. Soc.*, 1929, **6**, 473) we have shown that the relation between the incident radiation and the velocity of reaction between bromine and Rochelle salt, sodium formate and iodine, quinine sulphate and chromic acid can vary approximately from $\frac{1}{2}$ to 2. In the case of the reaction between potassium oxalate and iodine, the relation between intensity and velocity varies from $\frac{1}{2}$ to 1. We have carried on similar experiments with potassium oxalate and bromine using different amounts of potassium bromide which is a marked retarder in white light and in radiation of wave-length 7304 Å. The experimental arrangement is the same as described in previous papers. The following results have been obtained at 20°.

N/10-*Potassium oxalate and* N/100-*bromine* (10 *gm.* KBr *in* 100 *c. c. of* N/100-*bromine*), 10 *c. c. each*.

Diameter of the aperture.	k_1 Unimolecular.	k_1 After deducting the dark reaction : k_1 (*dark*) = 0·00205.
	A. *Source* :—*Sunlight.*	
2 cm.	0·0684	0·06635 (I)
0·8	0·0463	0·04425 (II)
0·4	0·0418	0·03975 (III)
	B. *Source* :—1000 *watt lamp.*	
2 cm.	0·0384	0·03635 (I)
0·8	0·0210	0·01895 (II)
0·4	0·0146	0·01255 (III)

N/10-*Potassium oxalate and* N/100-*bromine* (2 *gm.* KBr *in* 100 *c. c. of* N/100-*bromine*).

Diameter of the aperture.	k_1 Unimolecular.	k_1 After deducting the dark reaction : $k_1(dark) = 0{\cdot}00456$.
	C. *Source* :—1000 *watt lamp.*	
2 cm.	0·0770	0·0724 (I)
0·8	0·0400	0·0354 (II)
0·4	0·0254	0·0208 (III)
	D. *Region* :—$\lambda = 7304$Å.	
2 cm.	0·0203	0·0157 (I)
0·8	0·00976	0·0052 (II)
0·4	0·00693	0·00237 (III)

N/10- *Potassium oxalate and* N/100-*bromine* (1 *gm.* KBr *in* 100 *c.c. of* N/100-*bromine*).

	E. *Region* :—$\lambda = 7304$Å.	k_1 (*dark*) = 0·0194.
2 cm.	0·0609	0·0415 (I)
0·8	0·0300	0·0106 (II)
0·4	0·0229	0·0035 (III)

N/10-*Potassium oxalate and* N/100-*bromine* (0·75 *gm.* KBr *in* 100 *c.c. of* N/100-*bromine*).

	F. *Region* :—$\lambda = 7304$Å.	k_1 (*dark*) = 0·0365.
2 cm.	0·0814	0·0449 (I)
0·8	0·0460	0·0095 (II)
0·4	0·0394	0·0029 (III)

Ratio of velocities.	If proportional directly to the change in intensity.	If proportional to the square-root of the change in intensity.
	A. *Source* :—*Sunlight.*	
$\frac{I}{II} = \frac{0{\cdot}06635}{0{\cdot}04425} = 1{\cdot}5$	$\frac{3{\cdot}14}{0{\cdot}5024} = 6{\cdot}25$	$\sqrt{6{\cdot}25} = 2{\cdot}5$
$\frac{II}{III} = \frac{0{\cdot}04425}{0{\cdot}03975} = 1{\cdot}11$	$\frac{0{\cdot}5024}{0{\cdot}1256} = 4$	$\sqrt{4} = 2$
$\frac{I}{III} = \frac{0{\cdot}06635}{0{\cdot}03975} = 1{\cdot}67$	$\frac{3{\cdot}14}{0{\cdot}1256} = 25$	$\sqrt{25} = 5$

Ratio of velocities.	If proportional directly to the change in intensity.	If proportional to the square-root of the change in intensity.
B. *Source* :—1000 *watt lamp.*		
$\frac{I}{II}=\frac{0{\cdot}03635}{0{\cdot}01895}=1{\cdot}92$	$\frac{3{\cdot}14}{0{\cdot}5024}=6{\cdot}25$	$\sqrt{6{\cdot}25}=2{\cdot}5$
$\frac{II}{III}=\frac{0{\cdot}01895}{0{\cdot}01255}=1{\cdot}51$	$\frac{0{\cdot}5024}{0{\cdot}1256}=4$	$\sqrt{4}=2$
$\frac{I}{III}=\frac{0{\cdot}03635}{0{\cdot}01255}=2{\cdot}9$	$\frac{3{\cdot}14}{0{\cdot}1256}=25$	$\sqrt{25}=5$
C. *Source* :—1000 *watt lamp.*		
$\frac{I}{II}=\frac{0{\cdot}0724}{0{\cdot}0354}=2{\cdot}05$	$\frac{3{\cdot}14}{0{\cdot}5024}=6{\cdot}25$	$\sqrt{6{\cdot}25}=2{\cdot}5$
$\frac{II}{III}=\frac{0{\cdot}0354}{0{\cdot}0208}=1{\cdot}7$	$\frac{0{\cdot}5024}{0{\cdot}1256}=4$	$\sqrt{4}=2$
$\frac{I}{III}=\frac{0{\cdot}0724}{0{\cdot}0208}=3{\cdot}5$	$\frac{3{\cdot}14}{0{\cdot}1256}=25$	$\sqrt{25}=5$
D. *Source* :—$\lambda=7304$Å (1000 *watt lamp*).		
$\frac{I}{II}=\frac{0{\cdot}0157}{0{\cdot}0052}=3$	$\frac{3{\cdot}14}{0{\cdot}5024}=6{\cdot}25$	$\sqrt{6{\cdot}25}=2{\cdot}5$
$\frac{II}{III}=\frac{0{\cdot}0052}{0\,00237}=2{\cdot}2$	$\frac{0{\cdot}5024}{0{\cdot}1256}=4$	$\sqrt{4}=2$
$\frac{I}{III}=\frac{0{\cdot}0157}{0\,00237}=6{\cdot}6$	$\frac{3{\cdot}14}{0{\cdot}1256}=25$	$\sqrt{25}=5$
E. *Source* :—$\lambda=7304$Å (1000 *watt lamp*).		
$\frac{I}{II}=\frac{0{\cdot}0415}{0{\cdot}0106}=3{\cdot}91$	$\frac{3{\cdot}14}{0{\cdot}5024}=6{\cdot}25$	$\sqrt{6{\cdot}25}=2{\cdot}5$
$\frac{II}{III}=\frac{0\,0106}{0{\cdot}0035}=3$	$\frac{0{\cdot}5024}{0{\cdot}1256}=4$	$\sqrt{4}=2$
$\frac{I}{III}=\frac{0{\cdot}0415}{0{\cdot}0035}=11{\cdot}85$	$\frac{3{\cdot}14}{0{\cdot}1256}=25$	$\sqrt{25}=5$
F. *Source* :—$\lambda=7304$A (1000 *watt lamp*).		
$\frac{I}{II}=\frac{0{\cdot}0449}{0{\cdot}0095}=4{\cdot}73$	$\frac{3{\cdot}14}{0{\cdot}5024}=6{\cdot}25$	$\sqrt{6{\cdot}25}=2{\cdot}5$
$\frac{II}{III}=\frac{0{\cdot}0095}{0{\cdot}0029}=3{\cdot}24$	$\frac{0{\cdot}5024}{0{\cdot}1256}=4$	$\sqrt{4}=2$
$\frac{I}{III}=\frac{0{\cdot}0449}{0{\cdot}0029}=15{\cdot}5$	$\frac{3{\cdot}14}{0{\cdot}1256}=25$	$\sqrt{25}=5$

The experimental results show that the relation between intensity and the velocity of the reaction varies from 1/4 to 1 depending on the ratio of the light reaction and the thermal reaction. These results are in entire agreement with our conclusion that the relation between the intensity and velocity of a reaction is controlled by the ratio of light and dark reaction. In order to make sure that the absorption of radiation is proportional to the intensity of the incident radiation, we have determined the absorption of the incident radiation by a radiomicrometer and the results are as follows:

Diameter of the aperture.	Distilled water (deflection).	$N/10$-$K_2C_2O_4$ and $N/100$-Br_2 in 2 gms. KBr (deflection).	Difference in deflection.
2 cm.	37·1 cm.	34·1 cm.	3 cm.
0·8	6·1	5·65	0·45
0·4	1·55	1·45	0·1
Diameter of the aperature ...	2·0	0·8	0·4 cm.
Area	3·14	0·5024	0·1256 sq. cm.

Ratio of intensity.	Ratio of absorption.
$\frac{I}{II}=\frac{3·14}{0·5024}=6·25$	$\frac{3}{0·45}=6·66$
$\frac{II}{III}=\frac{0·5024}{0·1256}=4$	$\frac{0·45}{0·10}=4·5$
$\frac{I}{III}=\frac{3·14}{0·1256}=25$	$\frac{3}{0·1}=30$

Hence the amount of absorption of radiation of 7304Å by a mixture of potassium oxalate and bromine is directly proportional to the intensity of the incident radiation.

The foregoing results conclusively prove that the relation between velocity of the reaction between potassium oxalate and bromine in radiation of 7304 Å and both the intensity of the incident radiation and the amount of absorption can vary from 1/4 to 1 depending on ratio of the velocity of the dark and light reactions.

We are of the opinion that the velocity of this reaction as well as those of several other reactions may be proportional to $I^{\frac{1}{2}}$ in presence of strong light from a mercury lamp.

It will be interesting to note that the velocity of the reaction between hydrogen and bromine has been found to be proportional to the square-root of both the absorbed energy (Bodenstein and

Lütkemeyer, *Z. physikal. Chem.*, 1924, **114**, 208) and incident radiation (Briers and Chapman, *J. Chem. Soc.*, 1928, **133**, 1807). The same reaction appears to be directly proportional to the intensity (Briers and Chapman) of the incident radiation when the intensity is low.

Our results show that the reaction between potassium oxalate and bromine is markedly accelerated in the region 7304Å which cannot atomise the bromine molecules (6230Å is necessary to atomise bromine). Moreover, the relation between the velocity of a reaction and intensity is not always $\frac{1}{2}$; hence the conception of Berthoud (*Helv. Chim. Acta*, 1924, **7**, 307) that bromine molecules are atomised in light is not upheld by our experiments.

Summary.

(1) Experimental results show that the relation between the velocity of the reaction between potassium oxalate and bromine and the intensity of the incident radiation or the amount of energy absorbed can be varied approximately from 1/4 to unity, depending on the ratio of the thermal and photochemical velocities of the same reaction.

(2) By the absorption of radiation, chlorine, bromine, and iodine are not atomised in most cases but the molecules are activated by the absorption of incident energy and chemically react.

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Period of Induction in Chemical Reactions: Action of Hypophosphorous Acid on Copper Salts.

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It has been shown that period of induction is not confined to photochemical reactions, but is observable in several other reactions such as the action of acids on zinc, action of nitric acid on copper, action of acids on thiosulphates, and action of sulphurous acid on iodic acid. Recently Neogi and Neogi (*J. Chem. Soc.*, 1927, **131**, 30) have studied the period of induction in the interaction of mercuric chloride and sodium bicarbonate. Whilst preparing cuprous hydride by the interaction of hypophosphorous acid on copper sulphate, we observed that a distinct period of induction existed in this chemical reaction. Such a period was also observed in the case of the action of hypophosphorous acid on cupric chloride. It was, therefore, considered desirable to study these two instances of induction thoroughly.

It is to be noted at the commencement that no single cause can be uniformly assigned to all chemical reactions in which a period of induction can be observed. In the case of the action of hydrogen and chlorine, Chapmann and his co-workers (*Proc. Roy. Soc.*, 1925, **74**, 400 ; *J. Chem. Soc.*, 1906, **89**, 1399, and subsequent papers) have shown that minute traces of impurities are an important factor in causing the period of induction. So far as the interaction of sulphurous acid on iodic acid is concerned, Landolt (*Ber.*, 1886, **19**, 1317) has shown that the period of induction is due to successive intermediate reactions, which take place before iodine is finally liberated. Neogi and Neogi (*loc. cit.*) have shown that the period of induction in the interaction of sodium bicarbonate and mercuric chloride is similarly due to the formation of several intermediate compounds.

Now turning to the reactions under examination, the formation of cuprous hydride, by the interaction of hypophosphorous acid on copper sulphate, can never be due to the occurrence of a single reaction. The action of hypophosphorous acid on cupric chloride has also been shown here to be not merely a case of reduction of the cupric chloride to cuprous chloride, but really due to the formation of unstable intermediate compounds. It is, therefore, natural to presume that the period of induction in these cases

is mainly, if not solely, due to the formation of unstable intermediate compounds formed in successive reactions which take time before a visible reaction is observed. The nature of these intermediate reations would be discussed later on.

As regards the end products of the interaction between copper sulphate and hypophosphorous acid, Wurtz (*Compt. rend.*, 1844, **18**, 102) obtained cuprous hydride by treating the mixture below 70°. Bartlett and Merrill (*Amer. J. Sci.*, 1895, **17**, 195) also obtained the same hydride in a similar manner. Berthellot has stated that the hydride contains some basic cuprous phosphate as an impurity. Vorländer and Mayer obtained cuprous hydride by the action of sodium hyposulphite solution and dilute sulphuric acid on ccpper sulphate solution. Very recently Muller and Bradely (*J. Chem. Soc.*, 1926, **129**, 1669) have shown the undoubted existence of cuprous hydride, CuH.

As regards the end product of the action of hypophosphorous acid on cupric chloride, existing literature states that cuprous chloride is precipitated on warming. We have, however, prepared pure cuprous hypophosphite solution, which on simple heating yields cuprous hydride, but with excess of cupric chloride yields cuprous chloride. We are of opinion that the formation of cuprous chloride by the interaction of hypophosphorous acid on cupric chloride is not merely a case of reduction of the cupric chloride, but really a product of decomposition through stages to be discussed later on.

Experimental.

Action of Hypophosphorous Acid on Copper Sulphate.—Standard solutions containing known weights of copper sulphate and hypophosphorous acid were prepared. The strength of the hypophosphorous acid was ascertained by the iodine method (Sutton, "Volumetric Analysis," p. 317).

A measured volume of each solution, usually 10 c. c., was taken into two 50 c. c. boiling tubes of the same size and kept inmmersed in a thermostat and heated up to the temperature of the bath. The thermostat was often replaced by a water-bath, the water being contained in a capacious beaker (800 c. c.) and heated to the requisite temperature, which was maintained practically constant by means of a microburner. This is an excellent substitute for a thermostat, as the temperature could be kept within $\pm 1°$. The test tube containing the hypophosphorous acid solution was taken out from the bath and

the contents rapidly poured into the copper sulphate solution. By means of a standardised and throughly reliable stop-watch, the period of induction was read out, until a precipitate was just visible. The mixture was stirred only once every time by means of the thermometer dipped into the copper sulphate solution. A large amount of practice and repeated trials would be necessary in order to ensure the correct reading and the particular shade of the colour of the mixture, when the first visible reaction is observed. A dark background was used so that the required shade of the colour would be correctly read out each time.

The strength of the copper sulphate as well as of the acid solution was varied by taking measured volumes of their concentrated standard solutions and adding the requisite quantity of water. Readings of the stop-watch were taken after at first keeping the strength of the acid solution constant and varying the strength of the copper sulphate solution. The reversed process was also expreimented upon. Lastly the strengths of both the acid and the sulphate were varied.

Period of Induction in the Action of Hypophosphorous Acid on Cupric Chloride.

The period of induction in the interaction of cupric chloride and hypophosphorous acid, when cuprous chloride is precipitated, was next studied in detail. The results were similar to those obtained in the case of copper sulphate. Both sets of results are given side by side in each of the following tables.

TABLE I.

C_{Cu} = concentration of copper sulphate or chloride in gram. moles per litre. C_H = concentration of the acid.

Temperature = 70°. T = Induction period. $K = \dfrac{T - T_1}{\dfrac{C_1}{C} - 1}$.

Copper sulphate. $C_H = 0{\cdot}5023$.			*Cupric chloride.* $C_H = 0{\cdot}4812$.		
C_{Cu}	T (sec.)	K.	C_{Cu}	T (sec.)	K
0·0833	18	—	0·1667	35	—
0·0622	25	20·6	0·1429	43	48·4
0·0500	31	19·5	0·1334	47·5	50·0
0·0417	39	21·0	0·1250	51	47·9
0·0385	41·5	20·0	0·1177	55·5	49·2
0·0357	45	20·2	0·1112	60	50·0
0·0333	48	21·2	0·1053	63·5	48·9
0·0312	52	20·3	0·1000	67	47·9
0·0294	55	20·1	0·0953	71	48·0
0·0289	59	21·8	0·0909	75	47·9
	Mean	20·5		Mean	49·7

It would be observed from the above table that when the strength of the copper sulphate was getting weaker, the strength of the acid remaining constant, the period of induction was increasing, so much so that with $C_{Cu}=0{\cdot}0289$, the period of induction was three times as much as that when $C_{Cu}=0{\cdot}0833$. A similar result was obtained in the case of cupric chloride.

No simple proportionality as that of inverse ratio, however, is observable but an equation of the following nature can be worked out :—

$$T-T_1=K\left(\frac{C_1}{C}-1\right) \quad \text{or} \quad K=\frac{T-T_1}{\frac{C_1}{C}-1}$$

where C_1 and T_1 are initial concentration and the corresponding period of induction. The nature of K is the same in subsequent tables.

TABLE II.

Temperature = 70°.

Copper sulphate. $C_{Cu}=0{\cdot}2500$. *Cupric chloride.* $C_{Cu}=0{\cdot}5002$.

C_H	T (sec.)	K.	C_n.	T (sec.)	K.
0·5023	13	—	0.1925	275	—
0·4186	23	50·1	0·1782	342	835
0·3588	34	52·5	0·1718	375	829
0·3139	44	51·1	0·1659	408	829
0·2955	49	51·4	0·1604	440	825
0·2790	55	52·4	0·1552	474	827
0·2644	63	53·6	0·1504	512	846
0·2651	66	53·0	0·1458	540	828
0·2392	70	51·8	0·1415	574	829
0·2283	76	52·4	0·1375	613	845
		Mean 51·9			Mean 832

TABLE III.

Copper Salts and Hypophosphorous Acid.

Temperature=70°.

Copper sulphate.				*Cupric chloride.*			
C_H.	C_{Cu}.	T (secs.)	K.	C_{Cu}.	C_H.	T (sec.)	K.
0·5023	0·2500	13	—	0·5002	0·4812	50	—
0·4186	0·2083	18	25·0	0·3573	0·3437	78	70·0
0·3588	0·1786	24	27·5	0·3126	0·3007	92	70·0
0·3139	0·1562	29	26·6	0·2779	0·2673	105	68·7
0·2790	0·1389	34	26·2	0·2501	0·2406	118	68·0
0·2511	0·1250	40	27·0	0·2274	0·2187	130	71·9
0·2392	0·1190	42	26·3	0·2084	0·2005	145	67·8
0·2283	0·1137	45	26·7	0·1924	0·1851	158	67·5
0·2184	0·1087	48	26·9	0·1788	0·1718	170	66·8
0·2093	0·1042	51	27·1	0·1667	0·1604	185	67·6
		Mean	26·6			Mean	69·7

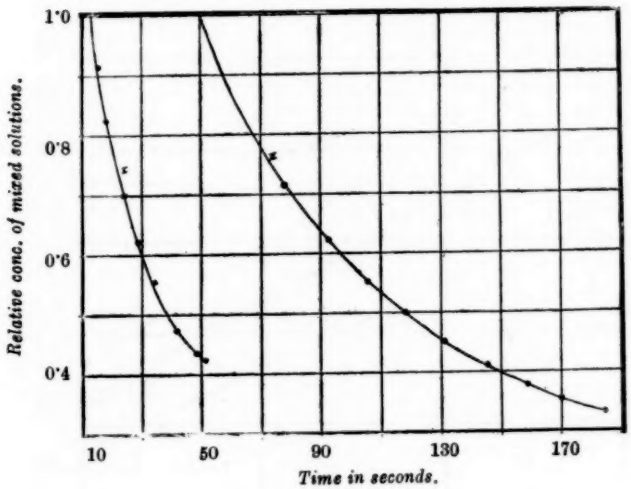

Fig. 1.

I = Copper sulphate. II = Cupric chloride

The effect of temperature on the period of induction was next studied, the solution being heated in a thermostat. With increasing temperature the period of induction decreases.

TABLE IV.

Copper sulphate.

$C_{CU}=0{\cdot}2500$. $C_H=0.2511$.

Temp.	...	50°	60°	70°	80°
T	...	53	27	13	6·5 secs

$C_{CU}=0{\cdot}5000$. $C_H=0{\cdot}2511$.

Temp.	...	50°	60°	70°	80°
T	...	66	40	24	13·5 secs.

$C_{CU}=0{\cdot}1250$. $C_H=0{\cdot}5022$.

Temp.	...	50°	60°	70°	80°
T	...	40	18	9	4 secs.

Cupric chloride.

$C_{CU}=0{\cdot}5002$. $C_H=0{\cdot}4814$.

Temp.	...	50°	60°	70°	80°
T	...	50	25	13	7 secs.

If the temperature be plotted against the logarithm of the period of induction, it is found that the points obtained can all be joined by means of a straight line (Fig. 2).

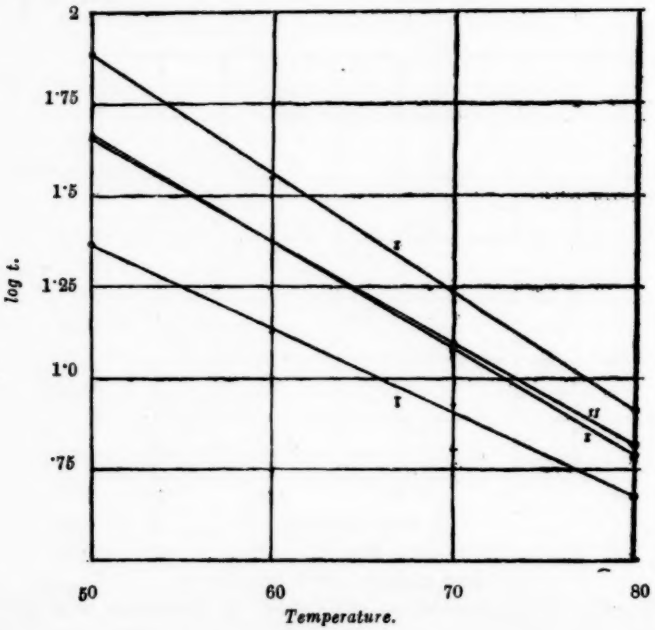

Fig. 2.

I = Copper sulphate. II = Cupric chloride.

The action of alcohols on the period of induction was next studied. A measured volume of alcohol was first added to the copper salt solution, the test tube being provided with a small spiral condenser, and heated to the requisite temperature in the bath. The condenser was then disconnected and the acid also previously heated to the same temperature in the bath was quickly poured and the condenser refitted.

It would be seen from the results tabled below that the period of induction increases with the addition of increasing volumes of methyl, ethyl, *n*-propyl and *iso*propyl alcohols. In the case of the two propyl alcohols, the period of induction is almost the same when equal volumes of the two alcohols are added. This fact is of interest in view of the observations of Neogi and Neogi (*loc. cit.*) regarding the period of induction in the interaction of sodium bicarbonate and mercuric chloride, when very wide divergences in the action of the two isomeric alcohols were observed.

TABLE V.

Copper sulphate.

Temperature = 50°.

Ethyl alcohol ...	... 0	1	2	4	6	8	10 c.c.	
T	... 70	88	90	95	102·5	115	135 secs.	
Methyl alcohol ...	... 1	2	4	6	8	10 c.c.		
T	... 86	89	93	99	107	121 secs.		
n-Propyl alcohol ...	... 1	2	4 c.c.					
T	... 87	93	95 secs.					
*iso*Propyl alcohol	... 1	2	4 c.c.					
T	... 90	92	94 secs.					

Cupric chloride.

$C_{Cu} = 0{\cdot}5002$. $C_{H} = 0{\cdot}4812$. Temp. = 70°.

Methyl alcohol ...	0	2	4	6	8	10 c.c.
T	50	54	59	60	60	60 secs.
Ethyl alcohol ...	2	4	6	8	10 c.c.	
T	54	63	75	79	80 secs.	
n-Propyl alcohol ...	2	6 c.c.				
T	54	71 secs.				
*iso*Propyl alcohol	2	6 c.c.				
T	53	73 secs.				

A little turbidity is produced by the addition of ethyl alcohol to the cupric chloride solution, which, however, disappears on the addition of the hypophosphorous acid.

The addition of different salts in the reacting mixture gave the following results.

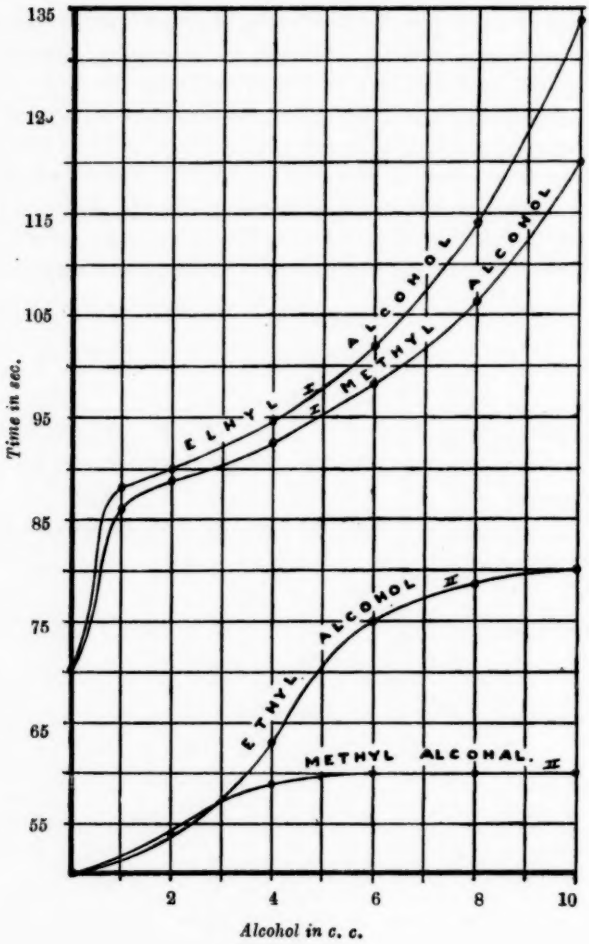

Fig. 3.

I = Copper sulphate. II = Cupric chloride.

On a study of the action of acids on the period of induction, it was found that hydrochloric acid gives a white precipitate of cuprous chloride, hence the action of sulphuric acid and nitric acid was studied. It was found that dilute acids cause an increase, while stronger acids cause a diminution in the period of induction.

TABLE VI.

Copper sulphate.

$C_{Cu}=0{\cdot}29000$. $C_H=0{\cdot}2009$.

Nitric acid (0·118*N*) ...	0	2	4	6	8	10 c.c.
T (at 50°)	70	80	90	101	112	120 sec.
Nitric acid (0·8501*N*) ...		2	4	6	8	10 c.c.
T (at 50°)		55	48	46	45	45 sec.
Sulphuric acid (0·114*N*) ...		2	4	6	8	10 c.c.
T (at 50°)		81	90	100	110	122 sec.

TABLE VII.

Cupric chloride.

$C_{Cu}=0{\cdot}5002$. $C_H=0{\cdot}4812$. Temp. = 70°.

Nitric acid (0·867*N*) ...	0	2	4	6	8	10 c.c.
T ...	50	36	30	29	30	29 secs.
Hydrochloric acid (0·867*N*)	2	2	4	6	8	10 c.c.
T ...	4	42	40	43	42 secs.	
Nitric acid (0·1 *N*) ...	0	2	4	6	8 c.c.	
T ...	73	82	91	101	108 secs.	

Neogi and Neogi (*loc. cit.*) found that in the case of sodium bicarbonate and mercuric chloride, the period of induction is influenced by the presence of salts. They, however, found that the influence on the period of induction is due to the anions and is independent of the cations. The same fact was observed by Berczeller (*Z. Biol.*, 1916, **2**, 444) in the case of the action of suphurous and iodic acids and is observed in this case also as the results recorded below will show. The similarity in the observation in all these three cases leads to the conclusion that the period of induction is due to anions and not to cations of a dissolved salt. Sulphates, nitrates, chlorides, citrates and tartrates were experimented upon and found to increase the period of induction. In the case of sodium chloride, a white precipitate of cuprous chloride was obtained and in the case of sodium citrate no precipitate was obtained even after 15 minutes, using 0·478 gms. The temperature was kept at 50° and equimolecular quantities of sodium and potassium salts were employed.

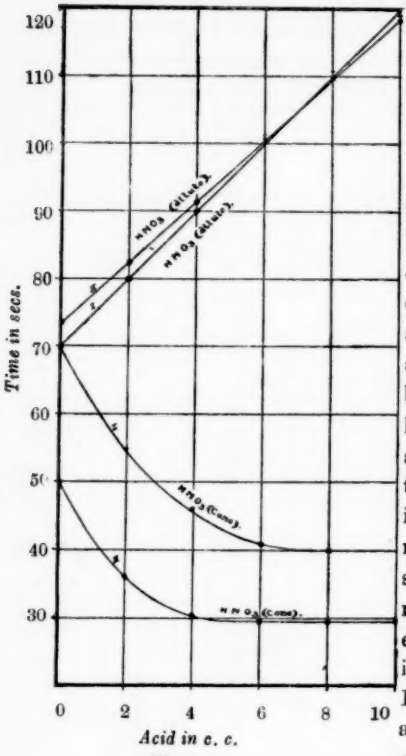

Fig. 4.
I=Cu SO_4. II=$CuCl_2$.

TABLE VII.

Temperature=70°.

Copper sulphate. $C_{Cu}=0·2000$. $C_H=0·2009$.			*Cupric chloride.* $C_{Cu}=0·5002$; $C_H=0·4812$.		
Salts.		*Period of induction.*	*Salt.*		*Period of induction*
0	gm.	53 secs.			
0·818	K_2SO_4	130	0 gm.	KNO_3	50 secs.
0·659	Na_2SO_4	135	0·646	,,	53·5

TABLE VIII—*contd.*

Salts.		*Period of induction.*	*Salts.*		*Period of induction.*
1·589 gm.	KNO_3	143 secs.	0·537 gm.	$NaNO_3$	53 secs.
1·322	$NaNO_3$	140	0·820	KCl	80
0·139	KCl	172	0·635	NaCl	84
0·107	NaCl	170	0·875	K_2SO_4	80
0·757	,,	No ppt. even after 30 mins.	0·714	Na_2SO_4	83
0·118	Na-tartrate	90			
0·0915	Na-citrate	135			
0·478	,,	No ppt. even after 15 mins.			
0·242	,,	The appearance of the ppt. begins at 85 secs. and is complete by 120 sec.			

Potassium and sodium oxalates as well as sodium tartrate produce turbidity to the solution. As sodium oxalate gives a precipitate with copper sulphate solution it was not used.

TABLE IX.

Temperature = 50°.

Copper sulphate. *Cupric chloride.*

$C_{cu}=0·2000$. $C_H=0·2009$. $C={}_{cu}0·5002$. $C_H=0·4812$.

Substance.	*Period of induction.*	*Substance.*	*Period of induction.*
0 c.c. glycerine	53 secs.	0 c. c. glycerine	73 secs.
4 ,, ,,	88	5 ,, ,,	80
6 ,, ,,	95	0·2176 gm. glucose	105
0·3095 gm. glucose	80	0·2076 ,, mannose	93
0·3096 ,, mannose	83	0·2076 ,, cane sugar	73

As regards the action of organic substances such as glycerine and sugars, it was found that cane sugar has no effect on the period of induction, whilst glycerine, glucose and mannose increase it. In the case of fructose, the appearance of the precipitate of cuprous hydride could not be detected owing to the dark green colour produced. In the case of fructose the appearance of the precipitate was not sharp.

Action of Light on the Reactions.

With a view to test whether the present reactions are photochemical or not, the experiments which were originally done in diffused light were repeated in a dark room provided throughout with red glass doors and windows. The electric lamps in the room were also covered with red glass covers. Solutions of copper sulphate, or chloride and hypophosphorous acid were prepared in the dark room itself and kept there for three days. The period of induction was noted after some trials in order to adjust vision in red light when the point at which precipitation commenced could be sharply read out with the help of a stop-watch and found to be the same in the dark and in different light. As the results are for comparison only, the concentrations of the acid have been only approximately determined.

TABLE X.

Copper Sulphate and Hypophosphorous Acid.

$C_{cv} = 0{\cdot}2500.$

C_H	T (Dark room).	T (Diffused light).
0·3100 (approx.)	47 secs.	49 secs.
0·2709 ,,	64·5	64

Cupric Chloride and Hypophosphorous Acid.

$C_{cv} = 0{\cdot}5002.$

0·4800 (approx.)	50 secs.	50 secs.
0·3600 ,,	100	102

Intermediate Stages in both the Reactions.

As regards the action of hypophosphorous acid on copper sulphate it has already been pointed out that cuprous hydride is formed below 80°. As the formation of such a simple compound as cuprous hydride by the interaction of copper sulphate and hypophosphorous acid could not evidently take place in one stage, we were at considerable pains to ascertain, if possible, the several stages through which

the reaction must proceed. We have been able to establish that copper hypophosphite is undoubtedly an intermediate product. In fact Wurtz supposed that copper hypophosphite remains in solution when hypophosphorous acid acts on copper sulphate.

We first attempted to prepare copper hypophosphite in a pure state. Silver hypophosphite, being very unstable, thallium hypophosphite, which has hitherto been unknown, was prepared by the interaction of hypophosphorous acid and thallous carbonate (separate communication). By the subsequent double decomposition between cupric chloride and thallium hypophosphite, copper hypophosphite was obtained in a pure condition in the solution, thallous chloride being precipitated. The solution, however, on concentration in a vacuum desiccator, decomposed and copper hypophosphite was therefore not obtained in a solid condition. The solution of copper hypophosphite, however, when heated alone to 70°—80° yielded a precipitate of cuprous hydride and when heated with cupric chloride yielded a white precipitate of cuprous chloride.

Preparation of pure Copper Hypophosphite Solution.—One gm. of thallium hypophosphite was dissolved in water and cupric chloride solution was added drop by drop, the mixture being thoroughly shaken. Thallous chloride was precipitated and when the mixture was vigouronsly shaken, the supernatent liquid became clear. The cupric chloride solution was added until the last drop did not produce any precipitate. The solution contained pure cuprous hypophosphite.

Pure copper hypophosphite solution was also prepared by double decomposition of recrystallised barium hypophosphite and copper sulphate when insoluble barium sulphate precipitated out and a solution of pure copper hypophosphite was obtained. The double decomposition of thallium hypophosphite and cupric chloride is to be preferred as a method of preparing pure copper hypophosphite solution as barium sulphate in the cold is very difficult to filter, and passes through the filter paper.

Decomposition of Copper Hypophosphite.—The solution of copper hypophosphite when gently heated in a water-bath at 70°—80° yielded the cuprous hydride in the same manner as the interaction of copper sulphate and hypophosphorous acid. Again, this solution of copper hypophosphite, when gently heated with cupric chloride solution, yielded a white precipitate of cuprous chloride in the same manner as in the interaction of cupric chloride and hypophosphorous acid.

In both cases a period of induction was observed as in the case when the free hypophosphorous acid was used.

It would thus be observed that copper hypophosphite $Cu(H_2PO_2)_2$ is an intermediate product in either of the two reactions, *viz.*, the action of hypophosphorous acid on copper sulphate and copper chloride.

We have further supposed that $Cu(H_2PO_2)_2$ is then decomposed into $CuH(H_2PO_2)$ and H_3PO_3, as a result of the study of the p_H values of the solution. This copper hydrogen hypophosphite in the case of the copper sulphate yields CuH and in the case of cupric chloride, Cu_2Cl_2. The reactions are represented below:—

In the case of copper sulphate—

$$CuSO_4 + 2H_3PO_2 = H_2SO_4 + Cu(H_2PO_2)_2$$
$$Cu(H_2PO_2)_2 + H_2O = H_3PO_3 + CuH(H_2PO_2)$$
$$2CuH(H_2PO_2) + 4H_2O = 2H_2PO_4 + 2CuH + 3H_2$$

In the case of cupric chloride—

$$CuCl_2 + 2H_3PO_2 = Cu(H_2PO_2)_2 + 2HCl$$
$$Cu(H_2PO_2)_2 + H_2O = H_3PO_3 + CuH(H_2PO_2)$$
$$CuH(H_2PO_2) + CuCl_2 + 2H_2O = 2CuCl + H_3PO_4 + 2H_2$$

Hypophosphorous acid is not a weak acid as was originally supposed. Though it acts as a monobasic acid the degree of its ionisation is quite high. Moreover as the reactions proceed with the ultimate precipitation of copper either as hydride or chloride, the forward reaction proceeds to the end.

Hydrogen Ion Concentration of a Solution of Copper Hypophosphite at 70°.

With a view to observe the process of the chemical reaction within the period of induction, the p_H value of the solution was determined. The method employed was a colorometric one, the electrometric method being not practicable as it requires a large interval of time between two determinations.

A solution of cupric hypophosphite was prepared; as this does not decompose at the ordinary temperature of the laboratory, the time necessary for filtration does not affect the period of induction.

The p_H values were known from the standard curves giving the relation between p_H values and different buffer mixtures

(Evers, *Analyst*, 1921, **46**, 397). The buffer solutions used by us were 0·1 *N*-sodium citrate and 0·1*N*-hydrochloric acid.

Twenty c.c. of each of the following solutions were mixed together and the precipitate was filtered out in Gooch crucibles. Thirty c.c. of the filtered solution were heated up to 60° in a thermostat and the p_H values were determined and 2 c.c. were drawn up each time and immediately chilled to arrest further reaction and then brought to the room temperature by rubbing the test-tube. In front of it was placed another test-tube containing one c.c. of the solution without the indicator in order to compensate for the colour of the solution.

TABLE XI.

$C_{Cu}=0·5020$. $C_{Ba}=0·2501$.

Time (min.)	0	10	20	30	40	50	60	65	70	75	77	79	81
p_H. ...	3·75	3·50	3·25	3·00	2·79	2·65	2·38	2·25	2·16	2·05	1·95	1·75	1·50

$C_{Cu}=0·5020$. $C_{Ba}=0·3002$.

Time (min.)	0	10	20	30	40	45	50	55	60	62	64	65	66·5
p . ..	3·50	3·35	2·92	2·62	2·36	2·25	2·12	2·00	1·90	1·83	1·75	1·62	1·59

Ten c.c. of $CuCl_2$ (0·5002 mol.) were added to 20 c.c. of a saturated solution of lead hypophosphite at 26°. The whole thing was cooled down to 0° and was filtered cold. 25 C.c. of the filtered solution were then heated to 70° and p_H values determined.

TABLE XII.

Time (min.) ...	0	2	4	6	7	8	8·30	9	9·30	9·45
p_H ...	3·1	2·85	2·57	2·25	2·15	2·00	1·90	1·75	1·44	1·25

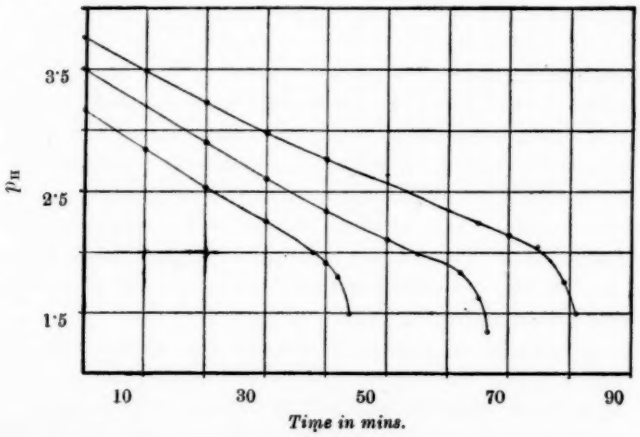

Fig. 5.

From the nature of the curves obtained by plotting the p_H values of both the reactions, which are similar to each other, it is seen that the upper part of the curves, which are of the nature of inclined straight lines, represents the stage in which phosphorous acid is produced whilst the lower part, in which the p_H values rapidly diminish, represents the stage at which the phosphoric acid is formed. This conclusively shows that the stages in which the two reactions have been shown to occur as exemplified in the equations given on page 542 are real ones. The precipitation comes up towards the very end of the inclined upper curve.

Discussion.

The following facts have been established in this paper, as a result of the study of the action of hypophosphorous acid on copper sulphate and of the same acid on cupric chloride.

(1) The period of induction depends on the concentration of the solutions, higher dilutions causing an increase in the period of induction.

(2) The period of induction decreases with rise of temperature.

(3) It increases in the presence of alcohols, glycerol, chlorides, sulphates, nitrates, oxalates, citrates, tartrates, some sugars, etc.

(4) It diminishes in the presence of acids (not very dilute).

Now turning to the causes that appear to determine the period of induction, it would be observed that it is due to the combined influence of the following factors:—

1. Influence of successive stages in the reaction (p. 542).
2. Change in temperature.
3. Catalytic influence of added substances.

Successive reactions. It would readily be understood that chemical reactions, occuring in successive stages, would have a period of induction during which time the successive reactions take place inside the system. "This is a necessary consequence of the law of mass action. The duration of the period depends on the relative magnitude of the velocity constants of the intermediate reactions." (Mellor, "Comprehensive Treatise in Inorganic and Theoretical Chemistry" 1922, Vol. II, p. 185).

Since the velocity of a chemical reaction is proportional to the mass of the reacting substances, the belated appearance of the cuprous hydride or chloride respectively, which is the period of induction, corresponds to the time necessary for the successive

reactions to take place before precipitation commences. The successive stages in which both the reactions take place have already been indicated.

Temperature. It has been shown that an increase of temperature causes diminution in the period of induction. This is due to the following causes:—

1. An increase of temperature increases the velocity of the intermediate reactions which would, therefore, result in decrease in the period of induction.

2. It increases ionisation with a resultant increase in the velocity of the intermediate reactions and thus diminishes the period of induction.

Influence of added substances. The influence of added substances, (*e.g.*, alcohols, glycerol, salts and acids) appears to be of a catalytic nature. As regards the action of acids the diminution of the period of induction is evidently due to the presence of a large number of hydrogen ions which act catalytically.

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Studies on the Effect of Ultra-violet Light on Colloids.

Part I.

By Panna Lal and P. B. Ganguly.

The effects of ultra-violet light and of radium and X-rays on colloidal solutions have been the subject of numerous investigations. In a previous paper (Ganguly and Dhar, *Kolloid Z.*, 1922, **31**, 16) one of us has shown that tropical sunlight is equally effective in coagulating colloidal solutions. In the case of certain colloids like colloidal gold, coagulation is brought about only after long exposure to ultra-violet light, whereas in the case of a number of other colloids, notably the metallic sulphides, coagulation is easily brought about by exposure to ordinary sunlight. Coagulation of colloids by heat is also known. Thus practically all kinds of radiation are capable of changing the size of colloidal particles.

No definite explanation of the mechanism of coagulation by light is yet available. There are two possible directions in which an explanation might be sought. The phenomenon might be an entirely physical one, where coagulation by light is merely a neutralisation of the charge on the particles, or it might be an altogether different process, where coagulation is mainly due to slow chemical changes in the system.

The effect of ultra-violet light on any solution would be the generation of electrons. As a result of this the bulk of the solution would be, for the time being, a seat of an extra positive charge. Coagulation of a negatively charged colloidal solution by ultra-violet light, might reasonably be explained as being due to the neutralisation of the negative charge on the colloid particles by the free positive charge in the solution. If this explanation be accepted it must necessarily follow that ultra-violet light should have no coagulating influence on positively charged colloidal solutions and should in every case coagulate negatively charged sols. The available experimental data, however, do not support the above view. In his monograph " Das Radium und Die Farben ", Doelter, as a result of numerous investigations on the action of radium and

ultra-violet rays, has shown that positively charged manganese, iron, chromium and aluminium hydroxide sols are visibly altered on exposure to ultra-violet light for a period of 2-6 hours. It has been found that a series of positively charged hydroxide sols like cerium, thorium and zirconium hydroxide sols are easily changed on exposure to ultra-violet light. Doelter also claims that a negatively charged sulphur sol was not coagulated by exposure to ultra-violet light, which, however, is doubtful in view of the observations of Raffo and Rossi (*Kolloid Z.*, 1912, **11**, 123). Thus experimental observations show beyond doubt that ultra-violet light can coagulate both positively and negatively charged colloids, its action being in no way limited to negatively charged sols.

Investigations on the coagulating action of radium rays have failed to throw any definite light on the problem. If the neutralisation of the charge on the particle, lay at the basis of the coagulation of colloids by different radium rays, one would expect, in that case, the negatively charged β-rays to coagulate only positively charged colloids and to have no influence on negatively charged sols. As will be seen, however, from the accompanying table,* there is no definite relationship between the sign of the charge on the colloid particle and the sign of the charge of the radium rays, which bring about coagulation.

The effect of β-rays on the coagulation of colloids.

Nature of the colloid.	Charge on the colloid.	Source of β-rays.	Observations.	Author.
Alkaline blood globulin.	Negative.	$RaBr_2$	Coagulation.	Hardy.
Acidified blood globulin.	Positive.	$RaBr_2$	No coagulation	Hardy.
Ferric hydroxide.	Positive.	0·1 gm. $RaBr_2$	No coagulation.	Henri & Meyer.
Silver sol.	Negative.	0·1 gm. $RaBr_2$	No coagulation.	Henri & Meyer.
Manganese, iron chromium and aluminium hydroxide sols.	Positive.	0·5 gm. $RaCl_2$	No coagulation.	Doelter.
Ferric hydroxide.	Positive.	—	Very slow coagulation.	Righi.
Silver sol.	Negative.	0·015 gm. $RaBr_2$.	No coagulation.	Jorrissen and Woudstra.
Chromium hydroxide sol.	Positive.	0·015 gm. $RaBr_2$.	Less stable towards electrolytes.	Jorrissen and Woudstra.

* A complete bibliography on this subject is given by Nordenson (*Z. physikal. Chem.*, 1915, **90**, 603).

Studies on the effect of X-ray radiations on colloids afford some evidence in favour of the charge neutralisation theory. Cl. ther and his co-workers (*Phil. Mag.*, 1927, **4**, 825; 1929, **7**, 86) have come to the conclusion that under the influence of X-ray radiations, negatively charged sols remain unaffected, whereas positively charged sols are invariably coagulated. Galecki (*Kolloid Z.*, 1912, **10**, 149), however, found an increase in the size of gold particles exposed to X-ray radiations, whereas Bhatnagar (*Indian Science Congress Abstracts*, 1929) in his recent experiments has failed to observe any coagulation with both positively and negatively charged copper sols. It is thus clear that in the absence of further experimental data, a definite conclusion on this point is difficult.

The chemical explanation of the coagulation of colloids by light is not without its supporters. Schaum (*Kolloid Z.*, 1914, **15**, 103) is of opinion that the action of light on colloids is not a physical process, but depends on a chemical change of either the dispersion medium, or of foreign substances, like traces of electrolytes, present in the colloid system. Similar views have also been expressed by Stintzing (*Koll. Chem. Beih.*, 1914, **6**, 231).

In the following experiments an attempt has been made to experimentally test the chemical view-point with regard to the coagulation of colloids by light. A number of colloidal solutions have been exposed to ultra-violet light from a mercury vapour lamp. The hydrogen ion concentration of the clear supernatant liquid after the hydrosols have been coagulated by light, has been determined. This value has been compared with the hydrogen ion concentration of the clear liquid obtained by ultra-filtration or by high speed centrifugalisation of a fresh sample of the same hydrosol. For acid solutions, the quinhydrone electrode was used to measure hydrogen ion concentrations, alkaline solutions being measured with the hydrogen electrode. The following experimental results were obtained.

Experimental.

Sulphide Sols.

Colloidal solutions of arsenic and cadmium sulphides were prepared by the usual methods and freed from hydrogen sulphide, as far as possible, by passing a current of hydrogen. Colloidal antimony sulphide was prepared from antimony potassium tartrate,

and after being treated with a current of hydrogen was further purified by dialysis. A colloidal solution of ferrous sulphide was prepared by passing a current of hydrogen sulphide through a dilute alkaline solution of ferrous sulphate, and was purified by dialysis. A part of each of these colloidal solutions was filtered through an ultra-filter, the filtration being repeated till a clear filtrate was obtained. Another part was exposed in a quartz tube to a mercury vapour lamp, the tubes being placed at a distance of 10 cm. from the lamp. The exposure was continued till the whole of the colloid was precipitated. The p_H values of the clear filtrates, before and after exposure, were determined and the following results obtained:—

Sol.	p_H (unexposed).	p_H (exposed).
Arsenic sulphide ...	4·70	3·31
Cadmium ,, ...	4·71	3·45
Antimony ,, ...	4·01	3·10
Ferrous ,, ...	6·53	7·60

Metallic Sols.

A colloidal solution of platinum was prepared by Bredig's method, and a sol of silver was prepared by Kohlschutter's process. A purple of Cassius sol was prepared by the addition of 10 c.c. of a 0·3% solution of gold chloride and 12·5 c.c. of a 0·5% solution of stannous chloride containing a slight excess of hydrochloric acid, to 200 c.c. of water. The dark violet precipitate obtained on standing was washed free from chlorides and finally peptised by boiling with weakly ammoniated water. The clear purple sol obtained by the above method was purified by dialysis. All these solutions were treated like the sulphides and the following values obtained:—

Sol.	p_H (unexposed).	p_H (exposed).
Platinum	5·85	5·68
Kohlschutter's silver ...	—	No coagulation.
Purple of Cassius ...	6·35	6·63

Sulphur Sols.

A colloidal solution of sulphur was prepared by adding a saturated solution of sulphur in alcohol to a large volume of water. Another sol of sulphur was prepared by slowly adding 50 c.c.

concentrated sulphuric acid to an equal volume of a 3*N*-sodium thiosulphate and purified by dialysis till the external water was free from sulphates. Both sols were coagulated on exposure and gave the following p_H values:—

Sol.	p_H (unexposed).	p_H (exposed).
Odèn's sulphur	6·42	2·24
Sulphur (by displacement of solvent). ...	6·43	6·17

Hydroxide Sols.

Colloidal solutions of cerium and thorium hydroxides were prepared by the dialysis of 10% solutions of ceric ammonium nitrate and of thorium nitrate respectively. A ferric hydroxide sol was prepared by the addition of a solution of ferric chloride to a large volume of boiling water, and purified by dialysis. After a day's exposure the sols were filtered and the p_H values of the filtrates measured: —

Sol.	p_H (unexposed).	p_H (exposed).
Cerium hydroxide ...	6·41	6·73
Thorium ,, ...	5·91	6·58
Ferric ,, ...	—	No coagulation.

Prussian Blue Sols.

The sol was prepared by the dialysis of a solution of Prussian blue in oxalic acid. The following p_H values were obtained:—

Sol.	p_H (unexposed).	p_H (exposed).
Prussian blue	5·96	6·11

Gum Mastic Sol.

The gum mastic sol was prepared by pouring an alcoholic solution of the gum in a large volume of water. The following p_H values were obtained:—

Sol.	p_H (unexposed).	p_H (exposed).
Gum mastic	6·31	6·04

Discussion of Results.

During the coagulation by light of arsenic, antimony and cadmium sulphide sols the following changes are observed : The sol first becomes turbid but retains its original colour, part of the sol is then precipitated, the colour becoming whitish. On further exposure practically the whole of the sulphide is precipitated, but the supernatant liquid is still a pale yellowish-white suspension. Finally all the solution is completely precipitated leaving a clear liquid. All these observations can be satisfactorily explained on the basis of chemical reactions brought about by exposure to ultra-violet light.

As is well-known, the sulphide sols owe their stability to the presence of hydrogen sulphide in the system, part of which is adsorbed on the surface of the colloid particles. Hydrogen sulphide in presence of water is easily oxidised on exposure to ultra-violet light generating sulphur acids. Two causes now contribute towards a diminution of the stability of the colloid: the coagulating action of the small amount of acid generated in the system, and the removal of a part of the stabilising ion by oxidation (Freundlich and Nathansohn, *Kolloid Z.*, 1921, **28**, 258). A part of the colloid is thus precipitated. A secondary reaction between the hydrogen sulphide and its products of oxidation produces sulphur in small concentrations which remains suspended as a sol. As the exposure is continued more of the sulphide is percipitated, generating a further amount of sulphur which forms a suspension in the beginning but finally gets precipitated when its concentration becomes sufficiently large. An analysis of the coagulum showed that it contained a quantity of sulphur which could be extracted easily by treatment with a suitable solvent. The supernatant liquid after total precipitation of the sol is fairly acidic as is shown by its p_H value.

Unlike arsenic sulphide, ferrous sulphide sol on exposure to light shows an increase in the p_H value of the filtrate after coagulation. Here, as in the case of other metal sulphides, stabilisation of the colloid is due to hydrogen sulphide. The primary action of light is to oxidise the hydrogen sulphide. This destruction of the stabilising electrolyte brings about the coagulation of the colloid. A secondary action now sets in between the iron sulphide and the sulphur oxide produced by the oxidation of hydrogen sulphide, whereby the latter products are all used up. The iron sulphide is converted into complex basic salts and precipitated as such (Berthelot and Gaudechon,

Compt. rend., 1911, **152**, 376). Ferrous sulphide does not develop an increased acidity like arsenic sulphide because of the above secondary reaction.

Bredig's platinum sol on exposure develops a slightly increased acidity. The nature of the particles in a Bredig sol is not clearly understood. The action of ultra-violet rays is probably the completion of the hydrolysis of the particles, which would account for the slightly increased acidity (*cf.* Eastlack, *J. Amer. Chem. Soc.*, 1915, **37**, 2667).

The sulphur sol prepared from sodium thiosulphate showed the most remarkable change in the p_H value after its coagulation by light. The acidity of the final filtrate was found to be due to sulphuric acid, which must have been generated, partly by the decomposition of the pentathionic acid adsorbed on the surface of the colloid particles, and, partly by the oxidation of the sulphur particles themselves. A very marked increase in the conductivity was observed by Raffo and Rossi (*loc. cit.*), when a similarly prepared sulphur sol was coagulated by light. The pronounced change in the p_H values, and in the conductivity as observed by Raffo and Rossi, establish beyond doubt that a series of chemical changes are brought about in the colloid system when it is exposed to light. It is not intended, however, in the present experiment, to follow the nature of these changes.

Colloidal solutions of cerium and thorium hydroxides when exposed to ultra-violet light show a decrease in the hydrogen ion concentration after exposure. A possible explanation for this decrease in acidity, on the basis of chemical reactions brought about by light may be as follows: Under the circumstances in which these hydroxide sols are prepared, they retain a small quantity of nitric acid which is not easily removed by dialysis. The sol sets to a jelly if the dialysis be carried too far, as has been shown by Fernau and Pauli (*Kolloid Z.*, 1917, **20**, 20) and also by Kruyt (*Rec. trav. chim.*, 1923, (*iv*), **42**, 1923). In all probability, a part of the acid is adsorbed on the surface of the colloid particles, and a part remains in solution in the dispersion medium, there being a certain equilibrium between the amount adsorbed and the amount in solution in the water. The primary action of ultra-violet light is to decompose a part of the acid present in the dispersion medium.* This disturbs

* The decomposition of concentrated nitric acid by light is well-known. Under the catalytic influence of the colloidal matter present in this system, even dilute

the equilibrium as a result of which a portion of the acid adsorbed on the surface of the colloid particles is given up to the aqueous medium, the colloid being rendered less stable than before. This process continues till the colloid begins to set. The reduced acidity is due to the partial decomposition of the nitric acid, which is the stabilising substance in the case of these colloids.

Prussian blue did not show any coagulation on exposure to ultra-violet light. The slight decrease in hydrogen ion concentration, after exposure, is probably due to the decomposition of the oxalic acid used to peptise the sol.

A gum mastic sol on exposure to ultra-violet light does not show any coagulation, but the filtrate after exposure shows a slight increase in the concentration of hydrogen ions. This effect is due to the same cause as produces a similar effect in the case of sulphur sol prepared by pouring a solution of sulphur in alcohol to a large volume of water. In both these cases the difference in the p_H values is due to the oxidation of the alcohol present in the system, the colloidal particles acting as catalysts for the above process.

In the case of practically all the colloids studied the p_H value of the filtrate of the unexposed sol has been found more or less different from the p_H value of the solution left after coagulation of the colloid by ultra-violet light. Most of the colloidal solutions studied have been purified, as far as possible, by dialysis and other methods. Consequently the electrolytes present in the colloid systems are mostly those which are either themselves adsorbed on the surface of the colloid particles or are subsequently generated by chemical actions on adsorbed ions and electrolytes. Since considerable differences in the p_H values have actually been obtained, it has to be admitted that chemical action does take place on exposure of colloids to light, mainly at the expense of adsorbed ions and electrolytes. In addition to the adsorbed electrolyte, the dispersed substance itself might undergo a change in its chemical nature. Although this does happen in a few cases, *e.g.*, in the case of ferrous sulphide, the behaviour is by no means a general one.

The sols studied during the present experiments were all hydrosols. On exposure to ultra-violet light, a chemical change in the dispersion medium, except for the formation of minute quantities of

nitric acid may reasonably be expected to be photochemically active (*cf.* Moore and Webster, *Proc. Roy. Soc.*, 1913, **87** [B], 163).

hydrogen peroxide, is not likely. This hydrogen peroxide, generated by the action of ultra-violet light on water, is probably not capable of bringing about a direct oxidation. When added to cerium hydroxide sol, hydrogen peroxide produced no direct change (Fernau and Pauli, *loc. cit.*), whereas in the case of a gold sol, hydrogen peroxide brings about a reduction of any oxidised particles to metallic gold (Nordensohn, *loc. cit.*).

It should be stated that the p_H values of the filtrates, as obtained in these experiments, are not absolute measures of the total hydrogenion contents of the system. In the total absence of chemical action, however, effects due to adsorption by the flocculated mass of precipitates should be the same in the case of coagulation by ultra-filtration as in the case of coagulation by light. Consequently except in the case of very fine colloids containing a large proportion of amicrons, observed differences in the p_H values will give a true indication as to whether a chemical action has taken place or not.

The stability and the charge of a colloidal solution are due to adsorbed ions. When a colloid is exposed to ultra-violet light, a chemical change sets in, which brings about a corresponding change in the hydrogen ion concentration of the colloid system. The chemical changes are at the expense of the ions or electrolytes adsorbed on the surface of the colloid particles. This results in the destruction of the stabilising influence of the adsorbed substances, and in the coagulation of the colloid. This fact lies at the basis of the coagulation of colloids by light. The above conclusion is supported by the recent experiments of Miss Roy and Dhar (*Indian Science Congress Abstracts*, 1929).

Further work is in progress.

Summary.

1. A number of colloidal solutions have been exposed to ultra-violet light and the p_H values of the clear filtrates, obtained before and after exposure, have been measured.

2. It has been found that both positively and negatively charged colloids are coagulated by ultra-violet light. These observations can not be satisfactorily explained on the basis of the physical theory of coagulation.

3. Distinct and well marked changes in the p_H values on exposure to ultra-violet light have been observed. Attempts have been made to interpret these in the light of known chemical and photochemical reactions.

4. The coagulation of colloids by ultra-violet light is due mainly to the destruction of the stabilising agents as a result of the chemical changes brought about by light.

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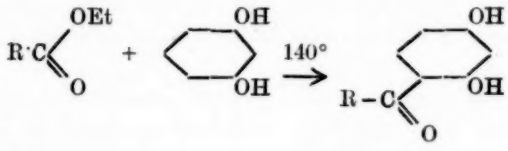
The Condensation of Esters with Resorcinol, Dimethylaniline and Diethyl-*m*-aminophenol.

By Rajendra Nath Sen and Ashutosh Mukherji.

Previously resorcinol and pyrogallol were condensed with methyl salicylate to produce compounds of the benzein series (Sen and Guha-Sarcar, *J. Indian Chem. Soc.*, 1924, **1**, 157). In elaboration of that reaction, benzoic ester has now been condensed with resorcinol at 180° in the presence of zinc chloride. Resorcinol benzein is produced with the intermediate formation of 2:4-dioxybenzophenone, which has also been now isolated. When heated to 140°, one molecule of resorcinol reacts with one of benzoic ester in presence of zinc chloride forming 2:4-dioxybenzophenone. In presence of excess of resorcinol and at 180° with the same condensing agent this intermediate compound forms the benzein, thus:



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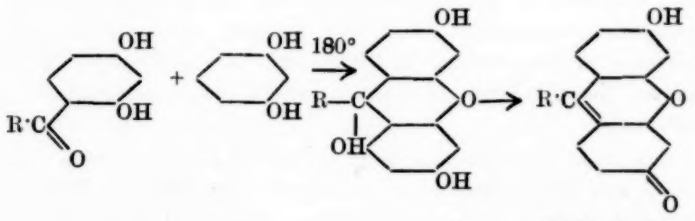


(Benzein stage).

The following esters have also been condensed with resorcinol:—*o*-nitro-, *o*-amino- and *p*-aminobenzoic esters; naphthoic ester; oleic and stearic esters. In the case of compounds which had previously been prepared by the condensation of aromatic acids with

phenols, it has been found that the condensations take place more readily and with greater yield when the acid is replaced by an ester.

The alkaline solutions of all the above compounds are deep red showing a beautiful green fluorescence on dilution. They dye yellow to orange shades while their bromo-compounds dye red shades. The flourescence is entirely subdued in the case of *o*-nitro-resorcinol benzein due to the effect of the nitro-group. On the other hand the nitro-group increases the reactivity of the ester as the condensation takes place at a lower temperature.

The fluorescence in the case of *o*- and *p*-aminobenzeins changes to a bluish shade on standing.

Resorcinol naphthalein exhibits similar fluorescence to resorcinol benzein but dyes deeper shades.

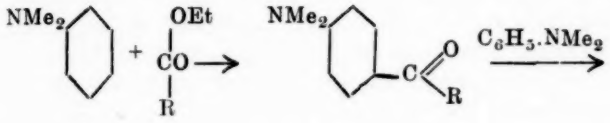
When the benzene ring is replaced by aliphatic residues having high molecular weights as in resorcinol olein and resorcinol stearein, the shade of the dye becomes deeper although the affinity to the fibre becomes less.

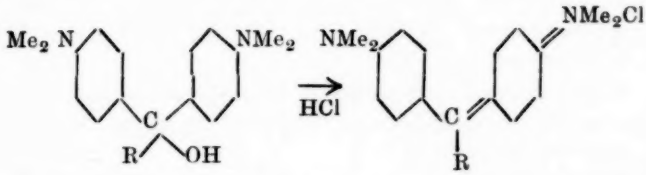
There is a remarkable difference in the solubility between the two compounds, olein and stearein, the former being insoluble in benzene ; and this fact has been utilised in separating the condensation products of the glycerides of the satuarated fatty acids in natural oils with resorcinol, from those derived from unsaturated fatty acids.

The natural oils (glycerides) being analogous to esters have been similarly condensed with resorcinol. Cocoanut oil, olive oil and castor oil have been made to yield dyes in this way producing yellow to brown shades on wool and silk, bright red shades being produced by the bromo-compounds. The easy methods of preparation, the cheapness of the starting materials and the high yields (80%) increase the possibility of these dyestuffs acquiring commercial importance.

Benzoic ester and its *o*-hydroxy-derivative have also been condensed with dimethylaniline, to give malachite green and *o*-hydroxy-malachite green. The nature of the condensing agent is very important. After the failure with zinc chloride (alone and in presence of gaseous hydrochloric acid) it has been found that a mixture of phosophorous oxychloride and zinc chloride brings about the desired reaction with satisfactory yield. The dye base is in each case formed directly, subsequent oxidation being not necessary.

This is the chief advantage of this new method of preparing the malachite green dyes. The reaction may be represented thus:—

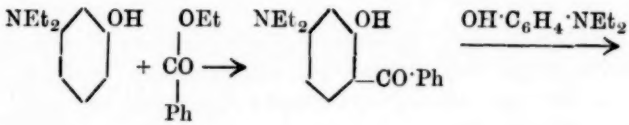


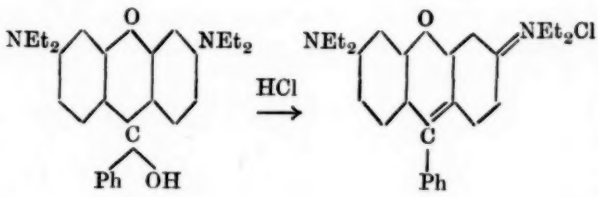


Malachite green was previously obtained by condensing dimethylaniline with benzoic acid (D.R.-P. 101426) but the yield, by using benzoic ester instead, is much more satisfactory.

Rhodamines have been obtained by the condensation of diethyl-*m*-aminophenol with benzoic, anthranilic and stearic esters in presence of zinc chloride.

The anthranilorhodamine is not a deeper dye than benzorhodamine while the rhodamine derived from stearine is a much feebler dye than benzorhodamine and resembles Pyronine G.





Experimental.

Resorcinol benzein.—Resorcinol (8 g.) and ethyl benzoate (7·5 c.c.) are heated with zinc chloride (10 g.) at 180° for 5 hours, dry hydrochloric acid gas being passed into the mixture. The product is

washed with hot water acidified with hydrochloric acid and then dissolved in caustic soda. After filtering, the solution is diluted to a large bulk in a basin, cooled in ice and neutralised with dilute acetic acid. After filtration, the product is dried and extracted with benzene, ether and chloroform and is finally crystallised as a yellow microcrystalline powder from dilute alcohol. It is then recrystallised from nitrobenzene. The substance is identical with resorcinol-benzein (Sen and Sinha, *J. Amer. Chem. Soc.*, 1913, **45**, 2985) (yield 80%) (Found: C, 73·8; H, 4·1. $C_{19}H_{12}O_3$ requires C, 79·16; H, 4·16 per cent.).

Monopotassium Salt.—Prepared as in the above paper (*loc. cit.*). Deep red fluorescent solid. (Found: K, 11·55. $C_{19}H_{11}O_3K$ requires K, 11·99 per cent.).

The *bromo*-derivative decomposes at 200°. (Found: Br, 52·5. $C_{19}H_8O_3Br_4$ requires Br, 52·98 per cent.).

Other compounds of the benzein series together with their derivatives are listed in the table on Benzeins.

2:4-*Dihydroxybenzophenone.*—Ethyl benzoate (1 mol.) and resorcinol (1 mol.) are heated with zinc chloride to 140° for 5 hours. The product is crystallised from hot water; yellow needles, m. p. 144° (yield, 10%); identical in every respect with 2:4-dihydroxybenzophenone. (*Annalen*, 1881, **210**, 256; *Ber.*, 1894, **27**, 1287; 1901, **34**, 2337) (Found: C, 72·5; H, 4·5. $C_{13}H_{10}O_3$ requires C, 72·9; H, 4·6 per cent.).

2:3:4-*Trihydroxybenzophenone.*—Ethyl benzoate (1 mol.) and pyrogallol (1 mol.) are heated with zinc chloride to 140° for 4 hrs. The product was purified by repeated crystallisations from hot water. Yellow needles, m. p. 140°; soluble in ether, alcohol and benzene (yield, 15%) (*Ber.*, 1890, **23**, 42; *Annalen*, 1892, **269**, 297). (Found; C, 67·0, 67·1; H, 4·8, 4·7. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·3 per cent.).

Benzeins.

Name.	Formula.	Preparation.	Appearance and m.p.	Analysis: Calc.	Found.	Properties.
Resorcinol-*o*-nitrobenzein.	$C_{19}H_{11}O_8N$.	*o*-Nitrobenzoic ester + resorcinol + $ZnCl_2$ at 140° for 4 hrs. Yield, 80%.	Yellow micro-crystalline. Does not melt up to 290°.	6·49 (N)	6·5%	Soluble in alcohol and acetone, very sparingly in chloroform, insoluble in ether. Brownish-yellow shades on wool and silk. Alkaline solution non-fluorescent.
Resorcinol-*o*-aminobenzein.	$C_{19}H_{13}O_5N$.	Anthranilic ester + resorcinol + $ZnCl_2$ at 180° for 6 hrs.	Softens near 175°.	4·6 (N)	4·6%	Identical with the same compound by Sen and Guha-Sarcar. (*J. Indian Chem. Soc.*, 1924, 1, 164).
Resorcinol-*p*-amino-benzein.	$C_{19}H_{13}O_5N$.	*p*-Aminobenzoic ester + resorcinol. Yield, 30%.	Decomposes at 290°.	4·6 (N)	4·6%	Red-green fluorescence in alkaline soln. changing to blue on standing. Soluble in alcohol, acetone, insoluble in ether, chloroform and benzene. Orange shades on wool and silk, deeper than the *o*-amino-compound.
Dibromo-derivative.	$C_{19}H_{11}O_5NBr_2$.	Bromination of the above compound.	Plates from alcohol.	34·7 (Br)	34·5%	Dyes wool and silk red shades.
Resorcinol naphthalein.	$C_{23}H_{14}O_5$.	Naphthoic ester + resorcinol. Yield, 80%.	Similar to resorcinol benzein. Does not melt up to 290°.	81·6 (C) 4·6 (H)	81·7% 4·6%	Similar to resoscinol benzein. Dyes deeper orange shades. Alkaline soln. shows red-green fluorescence.
Tetrabromo-derivative.	$C_{23}H_{10}O_5Br_4$.	Bromination of above.	Plates from alcohol. Decomposes at 260°.	48·9 (Br)	48·2%	Red shades on wool and silk
Resorcinol stearein.	$C_{54}H_{92}O_8$.	Stearic ester + resorcinol. Yield, 70%.	Softens at 150°.	80 (C) 9·33 (H)	79·6% 9·8%	Soluble in benzene (Sen and Guha-Sarcar, (*loc. cit.*).
Resorcinol olein.	$C_{50}H_{80}O_8$.	Oeic ester + resorcinol Yield, 80%.	Softens at 140°.	80·30 (C) 8·9 (H)	80·0% 9·2%	Soluble in alcohol (red-green), ethyl acetate (yellow) no fluorescence. Sparingly soluble in ether, insoluble in benzene, and petroleum ether. Orange shades on wool and silk.
Hexabromo-derivative.	$C_{50}H_{86}O_8Br_6$.	Bromination of above.		51·9 (Br.)	51·7%	Dyes wool and silk red shades.

Condensation of Natural Oils with Resorcinol.

Name of oil.	Preparation.	Appearance.	Analysis.	Properties.
Olive oil.	Olive oil (4 g.) + resorcinol (6 g.) + $ZnCl_2$ (4 g.) at 180° (4 hrs.). Separated into two fractions by benzene, in which the condensation products of the glycerides of the saturated fatty acids with resorcinol are soluble. Total yield, 80%. Purified from alcohol.	Brown amorphous powders (both fractions).	*Benzene fraction*: C, 70·3; H, 8·8% Resorcinol stearein requires C, 80; H, 9·3%. *Main fraction*: C, 75·7. H, 9·5%.	*Benzene fraction*: Similar to resorcinol stearein. Other fraction, soluble in alcohol (red-green), sparingly soluble in ether and insoluble in benzene. Dyes wool brownish shades.
Bromo-derivative.	Bromination of an alcoholic solution of the portion insoluble in benzene.	Red powder.	...	Dyes wool and silk red shades.
Castor oil.	Castor oil (6 g.) resorcinol (4 g.) at 180° with $ZnCl_2$. Purification as above.	Brownish powder.	...	Alcoholic and alkaline solns. fluorescent. Dyes wool and silk orange shades.
Bromo-compound.	Bromination of the above compound.	Red powder.	...	Dyes wool and silk red shades.
Cocoanut oil.	Oil (5 g.) + resorcinol (4 g.)	Brown amorphous powder.	...	Similar to the other compounds, but fluorescence deeper. Dyes wool and silk orange shades, brighter than any of the above products.
Bromo-compound.	Bromination of the above compound.	Red powder.	...	Dyes wool and silk red shades.

Triphenylmethane Dyes.

Name.	Formula.	Preparation.	Appearance and m.p.	Analysis. Calc.	Found.	Properties.
Malachite green.	$C_{27}H_{34}ON_2$.	Dimethylaniline (2 mols.) + ethyl benzoate (1 mol.) heated with an upright air condenser with $ZnCl_2$ and $POCl_3$ (6 hrs). Made alkaline with NaOH, distilled in steam till free from dimethylaniline, dissolved in boiling HCl and pptd. with NaOH. Purified from chloroform. Yield, 75%.	Semi-solid mass.	8·16(N)	8·0%.	Has all the properties of malachite green.
o-Hydroxy-malachite green.	$C_{23}H_{26}N_2O_2$.	Ethyl salicylate and dimethylaniline. Purification as above.	Bluish-green semi-solid mass.	7·74(N)	7·6%	Dyes wool and silk and tannined cotton bluish-green shades.

Rhodamines.

Benzorhodamine.	$C_{17}H_{22}O_3N_2$.	Diethyl-*m*-aminophenol (2 mols.) and ethyl benzoate (1 mol.) + $ZnCl_2$ at 160°, for 6 hrs. washed with hot water, dissolved in dil. HCl and pptd. with Na_2CO_3. Crystallised from absolute alcohol. Yield. 65%.	Violet powder, softens at 210°.	7·5 (N)	7·6%.	Alcoholic soln. exhibits violet fluorescence. Dyes wool, silk and tannined cotton bluish-red.
Anthranilorhodamine.	$C_{17}H_{23}O_2N_3$.	Ethyl anthranilate and diethyl-*m*-aminophenol. Yield, 70%.	Pink powder, softens at 225°.	9·74 (N)	9·6%.	Identical with same compound by Sen and Guha-Sircar, (*loc. cit.*).
Stearicrhodamine.	$C_{34}H_{54}N_2O_2$.	From ethyl stearate. Yield, 60%.	Red powder.	5·36 (N)	5·3%.	Soluble in ether, alcohol (violet fluorescence) and chloroform. Dyes wool, silk and tannined cotton pink shades.

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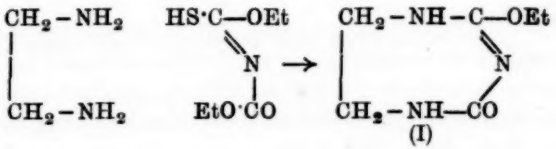
Formation of Heterocyclic Compounds from Ethyl carbethoxythiocarbamate.

By Praphulla Chandra Guha and Shanker Rao. A. Saletore.

Ethyl carbethoxythiocarbamate, $CO_2Et{\cdot}NH{\cdot}CS{\cdot}OEt$, was prepared by Delitsch (*J. pr. Chem.*, 1874, **9**, 464) by the action of ammonium sulphocyanide on chlorocarbonic ester in presence of alcohol. It contains two active ester groups—so, it was thought worthwhile to utilise this compound as a reagent for the building up of various types of heterocyclic compounds containing nitrogen, by condensing it with different kinds of organic bases, and to compare these results with those obtained by one of us (P.C.G., *J. Indian Chem. Soc.*, 1929, **6**, 65) in investigating the action of organic bases on a similar ester, *viz.*, diethyl xanthic formic ester $CO_2Et{\cdot}S{\cdot}CS{\cdot}OEt$. With this object in view, the action of ethylenediamine, *o*-phenylenediamine, hydrazine hydrate, phenylhydrazine, 4-phenyl-and 4-*p*-tolyl-thiosemicarbazides, di-*p*-tolylaminoguanidine, carbamide, thiocarbamide, aniline, *o*- and *p*-toluidines, α- and β-naphthylamines and benzidine has now been studied upon ethyl carbethoxythiocarbamate.

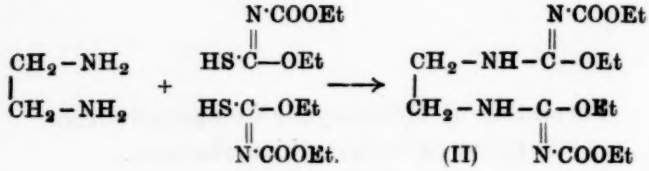
A molecule of the thiocarbamate reacting in the *cis*-thiol form with one molecule of ethylenediamine gives rise to 2-ethoxy-7-ketotetrahydro-1 : 3 : 6-heptatriazine, thus :—



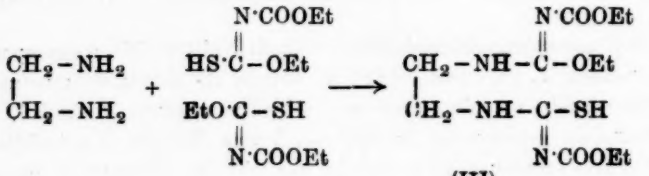
(I)

Together with this heptatriazine, which forms the major portion of the reaction product, there are also formed two open-chain compounds: (II) and (III), the formation of which evidently

depends on the fact that ethyl carbethoxythiocarbamate reacts with the diamine in the following two different manners:

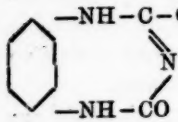


(II)



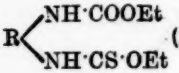
(III)

The compound (II) does not contain sulphur and is insoluble in alkali; whereas compound (III) contains sulphur and possesses mercaptanic properties. With *o*-phenylenediamine, the reaction proceeds to yield mainly the sulphur-free heptatriazine compound



(IV) analogous to compound (I).

Diethyl xanthic formic ester reacts with ethylene-and *o*-phenylenediamines to yield the corresponding monothiodiurethanes,

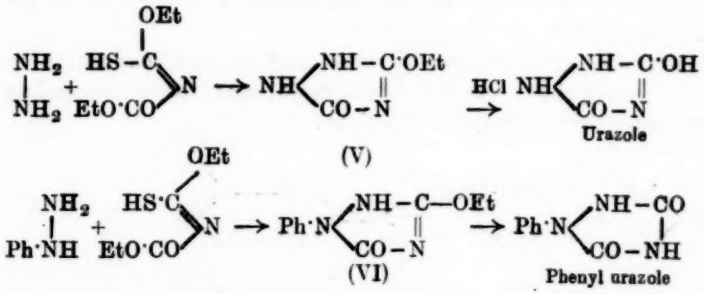


(R=phenylene and ethylene) which suffer internal condensation yielding phenylene and ethylene ureas and thioureas (*J. Indian Chem. Soc.*, 1929, **6**, 68).

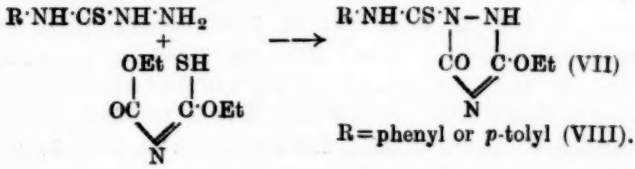
It might be mentioned in this connection that this is not the first occasion on which seven-membered ring compounds from 1:2-diamines have been made. Meyer prepared *o*-phenylene malonamide from *o*-phenylenediamine and malonic acid or ester (*Annalen*,

1903, **327**, 14, 26; 1906, **347**, 34, 45). Thiele and Steimmig prepared a seven-membered compound from *o*-phenylenediamine and acetylacetone (*Ber.*, 1907, **40**, 955). Ethylene and *o*-phenylene biguanides (Ziegelbauer, *Monatsh.*, 1896, **17**, 648; Dittler, *Monatsh.*, 1908, **29**, 645) are obtained from ethylene- and *o*-phenylene-diamines and dicyandiamides. Guha and De (*J. Indian Chem. Soc.*, 1926, **3**, 41) prepared a large number of heptatriazine compounds from *o*-aminophenylhydrazine.

A new method for the preparation of urazole derivatives has been found in the action of ethyl carbethoxythiocarbamate on hydrazine and phenylhydrazine : the reactions evidently proceed, thus:



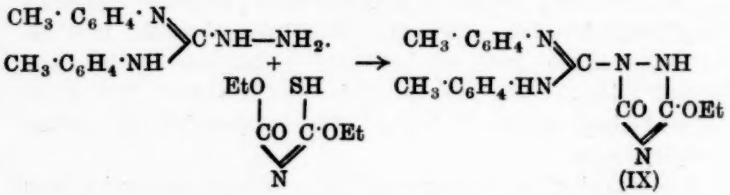
4-Phenyl- and 4-*p*-tolyl-thiosemicarbazides react with ethyl carbethoxythiocarbamate to yield 1:3:4-triazole derivatives, which in a sense may be regarded as urazoles.



R=phenyl or *p*-tolyl (VIII).

A close examination of the above reaction will reveal the fact that for the formation of these urazole derivatives the hydrazine part of the semicarbazides only takes an active part ; to this extent these reactions resemble the formation of urazole derivatives from hydrazine and phenylhydrazine mentioned earlier. An analogous case is to be found in the action of semi- and thiosemi-carbazides upon acetoacetic ester as studied by De (*J. Indian Chem. Soc.*, 1926, **3**, 30). The action of ditolylaminoguanidine on the thiocarbamate has also been studied with the result that in this case also the

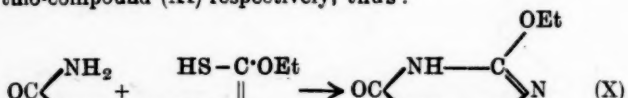
hydrazino-part of the guanidine reacts like that of phenylhydrazine and thiosemicarbazides to yield a urazole derivative, thus: –



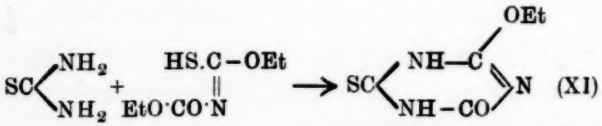
(IX)

Diethyl xanthic formic ester, however, reacts with phenylhydrazine, and 4-R-thiosemicarbazides to yield the corresponding carboxylic esters Ph·NH·NH·CS·OEt and RNH·CS·NH·NH·COOEt) respectively (*ibid*, pp. 66, 72).

Urea and thiourea react with ethyl carbethoxythiocarbamate to yield 6-ethoxy-2:4-dioxy-1:3:5-triazine (X) and the corresponding thio-compound (XI) respectively, thus:



(X)

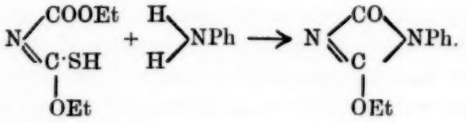


(XI)

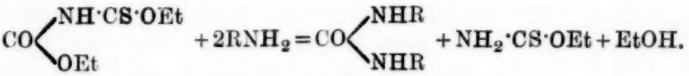
Oxy derivatives of 1:3:5-triazines have been synthesised by Pinner (*Ber.*, 1 90 **23**, 2919; 1892, **25**, 1424), Ephraim (*Ber.*, 1897, **30**, 2009), and Rapperfort (*Ber.*, 1901, **34**, 1900) by the action of phosgene on aryl amidines. 2:4-Dioxy-1:3:5-triazines have been prepared by Nencki (*Ber.*, 1876, **9**, 234), Kolb (*J. pr. Chem.*, 1891, **49**, 97), Ostrogorich (*Annalen*, 1895, **288**, 318; *Gazzetta*, 1897, **27**, 2, 41) by heating acetyl urethane with urea (or acetyl urea with urethane). 2:4:6-Trioxy-1:3:5-triazine (cyanuric acid) and its oxy- and *N*-alkyl derivatives are also known (Meyer and Jacobson, "Lehrbuch der Organischen chemie," Vol. I, Part 2, pp. 1331-1336). 2:4:6-Trimercapto-1:3:5-triazine (trithiocyanuric acid) was prepared by Troger and Hornung (*J. pr. Chem.*, 1898, **57**, 357) and by Johnson and Menge (*J. Amer. Chem. Soc.*, 1904, **32**, 362, 370).

By analogy with the formation of ring-compounds as described above it was expected that ethyl carbethoxythiocarbamate migh react with aromatic amines to yield four-membered heterocyclic compounds

with alternate carbon and nitrogen atoms according to the following scheme:—



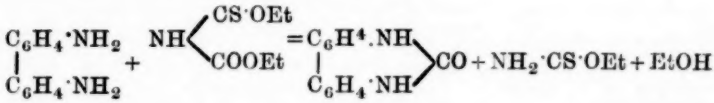
But actually the reaction has been found to proceed in quite a different manner giving rise to sym.-disubstituted ureas, thus:—



(XII to XVI)

$$NH_2{\cdot}CS{\cdot}OEt \xrightarrow{\text{Heat}} Et{\cdot}SH + HCNO \text{ (and cyanuric acid).}$$

Benzidine similarly gives carbonylbenzidine, but as it contains two amino-groups in the same molecule, one molecule of the thiocarbamate reacts with one molecule of it, thus:—



Diethyl xanthic formic ester reacts with the aromatic amines to yield the corresponding thiodicarbomonothiodiaryl amides RNH·CS·S·CO·NHR (Guha and Dutt, *ibid*, p. 65).

Experimental.

Ethyl carbethoxythiocarbamate required for these experiments was conveniently prepared in quantity by the method of Delitsch (*J. pr. Chem.*, 1874, **10**, 118). As described by him the substance is obtained as pale *yellow* prismatic crystals, m. p. 43° ; whereas, according to Doran (*J. Chem. Soc.*, 1896, **69**, 334) the ester comes out from solutions in rossettes of *yellowish* needles, m. p. 44—45°. We, however, found that repeated crystallisations from light petroleum yielded a pure *white* product which was needle-shaped and melted at 46°. The substance could also be purified more easily, by treating the potassium salt with dilute hydrochloric acid in aqueous solution.

The *potassium* derivative was prepared by dissolving the crude ethyl carbethoxythiocarbamate (160 g.) in cold absolute alcohol and by adding to it a concentrated alcoholic solution of caustic potash under ice cooling till there was no more separation of any solid. The salt was filtered on the pump, washed with cold alcohol and crystallised from 92 per cent. alcohol ; m. p. 225°, yield, 120 g. It is soluble in water and hot alcohol.

Ethyl Carbethoxythiocarbamate was isolated from the potassium salt by dissolving the latter in the minimum quantity of water and adding dilute hydrochloric acid. The pale yellow precipitate was crystallised from petroleum (b. p. 60-80°) as white crystalline needles, m. p. 46° easily soluble in alcohol and ether and also in hot water ; (Found : N, 7·8 ; S, 17·89. $C_6H_{11}O_3NS$ requires N, 7·9 ; S, 18·08 per cent.).

Methyl Derivative.—The potassium salt of the thiocarbamate in alcoholic solution was heated on the water-bath with a slight excess of methyl iodide under reflux for about half an hour when crystals of potassium iodide separated out. After filtration, the solution was made free from any excess of methyl iodide by heating on the water-bath, and water was then added to it when an oily product separated out, which solidified on cooling and crystallised from dilute alcohol ; m. p. 32-33°. It is extremely soluble in alcohol. (Found : N, 7·4. $C_7H_{13}O_3NS$ requires N, 7·32 per cent.).

The *benzyl* derivative was obtained by heating an alcoholic solution of the potassium salt (5 g.) and benzyl chloride (3 g.) for two hours on a water-bath. The precipitated potassium chloride was removed and the filtrate freed from alcohol. The residual oily product was then taken up in ether, washed with water, dried over calcium chloride and the ether distilled off. The white solid thus obtained was crystallised from petroléum (b. p. 60-80°) in plates, m. p. 45-46°. It is readily soluble in alcohol. (Found : N, 5·3. $C_{13}H_{17}O_3NS$ requires N, 5·24 per cent.).

Reaction with Ethylenediamine : Formation of Compounds (I), (II) *and* (III).—On mixing ethyl carbethoxythiocarbamate (6 g.) with ethylenediamine (3 g.) a vigorous reaction took place with development of much heat and liberation of sulphuretted hydrogen. The hot molten mass solidified on cooling. This was treated with a dilute solution of caustic alkali, when a portion dissolved. The residue was boiled with alcohol (95 per cent.) and filtered. On being cooled

the filtrate deposited a white crystalline product (I) which was recrystallised from alcohol in needles, m. p. 218°. It is soluble in hydrochloric acid from which solution it is precipitated by alkali, it is sparingly soluble in hot water. It was proved to be free from sulphur. (Found: N, 26·8. $C_6H_{11}O_2N_3$ requires N, 26·7 per cent.)

Treatment with Hydrochloric acid.—The Compound I (3 g.) was heated on a water-bath with 30-40 c. c. of 6*N*-hydrochloric acid when there was noticed a copious evolution of gas. On cooling however, only 0·2 gm. of a white crystalline solid separated which after recrystallisation from dilute alcohol melted at 225° and was found to be insoluble in acids but soluble in alkalis. It contains 19·5 per cent. of nitrogen which agrees fairly well with the formula of ethylene dicarbamic acid.

Compound (II).—Further concentration of the mother-liquor from the above gave rise to a small quantity of a white crystalline product (m. p. 101-102°) insoluble in alkalis. It crystallises easily from alcohol and does not contain any sulphur. (Found: N, 15·8. $C_{14}H_{26}O_6N_4$ requires N, 16·1 per cent.). As the amount of the product was small no further work could be done on it.

Compound (III).—The alkali extract of the reaction mixture, on being treated with dilute hydrochloric acid, precipitated a white flocculent solid, which redissoved on the addition of more acid. It was, however, obtained from the acid solution by careful addition of sodium carbonate solution and was crystallised from water in needles, m. p. 123°. (Found: C, 44·23 ; H, 6·92 ; N, 16·9 ; S, 9·59. $C_{12}H_{22}O_5N_4S$ requires C, 43·11 ; H, 6·58 ; N, 16·8 ; S, 9·58 per cent.).

2-*Ethoxy*-4:5-*benzo*-7-*keto*-*tetrahydro*-1:3:6-*heptatriazine* (IV).—Ethyl carbethoxythiocarbamate (6 g.) was condensed with *o*-phenylenediamine (3·6 g.) as described in the previous experiment, with this modification, however, that for completion of the reaction, the reaction mixture was heated for about half an hour on the water-bath. But in this case only one product was obtained, which crystallised slowly from dilute acetic acid. It was very difficultly soluble in alcohol, easily in glacial acetic acid and almost insoluble in most other organic solvents. It does not contain sulphur and melts at about 330°; yield, 5 g. (Found : N, 20·48. $C_{10}H_{11}O_2N_3$ requires N, 20·48 per cent.).

3-*Keto*-5-*ethoxy*-*dihydro*-1:2:4-*triazole* (V).—Ethyl carbethoxythiocarbamate (3 g.) was mixed with hydrazine hydrate (1 g.) when there was a considerable development of heat and liberation of

sulphuretted hydrogen. The product, at first a liquid, partially solidified when it was heated on the water-bath from two to three hours, by which time the evolution of sulphuretted hydrogen ceased. The product was next boiled with alcohol and filtered. The filtrate on cooling yielded a white substance, which was crystallised from the same solvent in needles, m. p. 170-172°. It is moderately soluble in cold water and alcohol and excessively so in hot water. It does not contain sulphur. (Found: N, 32·11. $C_4H_7O_2N_3$ requires N, 32·5 per cent.). On boiling for a long time with water or for a short time with hydrochloric acid the ethoxyurazole is hydrolysed to urazole, m. p. 244°.

3-Keto-2-phenyl-5-ethoxy-dihydro-1:2:4-triazole (VI).—When phenylhydrazine (2 g.) was added to ethyl carbethoxythiocarbamate (3·5 g.) there was evolution of sulphuretted hydrogen even in the cold. The mixture was then heated on the water-bath under reflux for nearly two hours, by which time the liberation of sulphuretted hydrogen completely ceased, and a solid product was seen to have been formed. It was cooled and filtered on the pump, washed with a little alcohol and crystallised from the least quantity of alcohol in needles, m. p. 150-151°. Yield, 0·5 g. (Found: N, 20·23. $C_{10}H_{11}O_2N_3$ requires N, 20·48 per cent.). It is very soluble in alcohol and water and does not contain sulphur. When heated with hydrochloric acid for a few minutes it is converted into Pinner's phenylurazole, m. p. 263°.

3-Keto-2-carbothiophenylamido-5-ethoxy-dihydro-1:2:4-triazole (VII).—On heating 4-phenylthiosemicarbazide (4 g.) with the thiocarbamate (4 g.) under reflux in an oil-bath at 140°, sulphuretted hydrogen was given off. After three hours' heating the action subsided. The molten mass solidified, on cooling when it was triturated with cold alcohol and crystallised twice from the same solvent in glistening white needles, m. p. 246—248°. Yield, 3 g. (Found: N, 20·92. $C_{11}H_{12}O_2N_4S$ requires N, 21·2 per cent.).

3-Keto-2-carbothio-p-tolylamido-5-ethoxy-dihydro-1:2:4-triazole (VIII).—Ethyl carbethoxythiocarbamate was condensed with 4-*p*-tolylthiosemicarbazide just as in the case of 4-phenylthiosemicarbazide, and a product with similar properties melting at 186-187° was obtained. It was however found to be more soluble in alcohol. (Found: N, 20·23. $C_{12}H_{14}O_2N_4S$ requires N, 20·14 per cent.).

2-Di-p-tolylamidino-3-keto-5-ethoxy-dihydro-1:2:4-triazole (IX).—Di-*p*-tolylaminoguanidine (2·5 g.) was heated with the thiocarbamate

(1·8 g.) without any solvent for about half an hour when the whole thing solidified. The solid after filtration and washing with alcohol was crystallised from the same solvent in rectangular plates, m. p. 229-230°. Yield, 2 g. It is soluble in alcohol and in hydrochloric acid. (Found: N, 19·75. $C_{19}H_{21}O_2N_5$ requires N, 19·94 per cent.). On heating with hydrochloric acid for some time it passed into solution, which yielded on neutralisation with dilute caustic soda solution a solid substance. On crystallisation from alcohol it was obtained in short fine needles, m. p. 256-257° (decomp.).

2-*Ethoxy*-4:6-*diketo*-3:4:5:6-*tetrahydro*-1:3:5-*triazine* (X).—Urea (1·2 g.) and the thiocarbamate (3·5 g.) were heated together when sulphuretted hydrogen was evolved. After 3-4 hours' heating the molten mass assumed a turbid appearance, when it was cooled in ice and scratched with a glass rod upon which a solid separated. This was filtered, washed carefully with alcohol and then crystallised from dilute alcohol in tiny white needles, m. p. 171-173°. Yield, 0·9 g. (Found: N, 27·63. $C_5H_7O_3N_3$ requires N, 27·4 per cent.). It is soluble in water and alcohol and is free from sulphur.

2-*Ethoxy*-4-*thio*-6-*keto*-3:4:5:6-*tetrahydro*-1:3:5-*triazine* (XI).—Thiourea (1·5 g.) dissolved in the least quantity of water and a few drops of alcohol was heated with the thiocarbamate (3·5 g.) till sulphuretted hydrogen was no longer given off. The pasty liquid, on cooling and scratching with a glass rod, gave rise to a small amount of a white solid, which crystallised from alcohol. The product shrinks at 110° and melts at 150°. Repeated crystallisations did not alter the m. p. It is soluble in water and alcohol. Yield, 0·5 g. (Found: N, 24·14. $C_3H_7O_2N_3S$ requires N, 24·2 per cent.)

Reaction with Aniline: Formation of Diphenylurea (XII).—Ethyl carbethoxythiocarbamate (3 g.) was heated with aniline (1·5 g.) under reflux for an hour, when there was effervescence with the liberation of a gas smelling of mercaptans. The flask was cooled when white crystals were found to have been formed, which were filtered on the pump, washed with benzene, dried and crystallised from absolute alcohol in white glistening needles, m. p. 235°. (Found: N, 13·29. $C_{13}H_{12}ON_2$ requires N, 13·25 per cent.) The substance was proved to be diphenylurea by taking its mixed m. p. with a genuine sample prepared from urea and aniline (Baeyer, *Annalen*, 1864, **131**, 252).

Reaction with p-*Toluidine* : *Formation of Di-*p-*tolylurea* (XIII).—Ethyl carbethoxythiocarbamate was condensed with *p*-toluidine when a white product was obtained; m. p. 270°. (Found : C, 74·83 ; H, 6·3 ; N, 11·71. $C_{15}H_{16}ON_2$ requires C, 75·0 ; H, 6·7 ; N, 11·71 per cent.).

Reaction with o-*Toluidine* (XIV).—o-Toluidine in a like manner gave the corresponding di-*o*-tolylurea as white crystalline needles from alcohol, m. p. 246-247°. (Found : N, 11·8. $C_{15}H_{16}ON_2$ requires N, 11·7 per cent.).

Reaction with α- and β-Naphthylamines : *Formation of* (XV) *and* (XVI).—When a mixture of ethyl carbethoxythiocarbamate (2 g.) and *α*-naphthylamine (3 g.) was heated at 160°, there was effervescence. The heating was continued for an hour during which time the reaction was complete and the molten product was found to have become solid. A small quantity of the adhering tarry product was removed by triturating it several times with benzene and hot alcohol and it was finally crystallised from glacial acetic acid ; m. p. 295 296°. (Found : N, 8·9. $C_{21}H_{16}ON_2$ requires N, 8·97 per cent.)

Similarly, with *β*-naphthylamine the corresponding di-*β*-naphthylurea was obtained crystallising from glacial acetic acid in needles. m. p. 309-310°.

As there seems to be a good deal of difference in the melting points ascribed to *αα'*-dinaphthylurea—[Delbos, *Annalen*, 1847, **64**, 370 ; Zinnin, *Annalen*, 1859, **108**, 229 ; Schiff, *Ber.*, 1879, **12**, 385 ; Huhn, *Ber.*, 1885, **19**, 2405 (m. p. 270°) ; Young, *J. Chem, Soc.*, 1897, **71**, 1201 (284-286°); Vittenet, *Bull. Soc. Chim.*, 1874, **21**, 950 (314-315°) ; Walther and Wldkowski, *J. pr. Chem.*, 1898, **59**, 278, (295-296°)] as also in those of the corresponding *ββ'*-compound [Huhn (293°) ; Walther and Wldkowski (300°) ; Young, *J. pr. Chem.*, **1899, 60**, 256 (289-290°); Vittenet (309-310°); Ekstrand, *Ber.*, 1887, **20**, 1360 (286°)], these two compounds were prepared by two different methods, *viz.*, those of Vittenet and of Young. The products obtained were carefully freed from adhering impurities and were repeatedly crystallised from glacial acetic acid. The *α*-compound obtained by either method melted at 295-296° and the *β*-compound at 309-310°. The mixed m. p. of these substances taken with the corresponding substances prepared by our method from the thiocarbamate showed no lowering.

Reaction with Benzidine : *Formation of Carbonylbenzidine* (XVII).—The thiocarbamate (1 mol.) was heated with benzidine (1 mol. and

a little more) when after a time a solid separated, which was filtered, washed with alcohol and dried. It is very sparingly soluble in alcohol and acetic acid and is insoluble in all other common organic solvents. Hence, the substance could not be crystallised. It begins to get brown at 250° and blackens at about 300°. Yield, 3 g. (Found: N, 13·85. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.). This compound was prepared by Michler and Zimmermann (*Ber.*, 1881, **14**, 2178) by the action of phosgene on benzidine and properties similar to those of our compound were attributed by them to it.

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Constitution of the Active Principle of *Embelia Ribes*. Part I.

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Embelia ribes, or *Vidanga* as it is known in Bengali and Sanskrit, and *Baberang* in Hindustani, has been known in Hindu Materia Medica for a very long time. Charaka describes the fruit as tonic and soothing for the digestive system and recommends its use in dyspepsia, flatulence, gripes, etc. Sushruta describes the fruit as anthelmintic, alterative and tonic and recommends its use along with liquorice root for the purpose of strengthening the body and preventing the effect of age. Later writers regard it as carminative, stomachic, anthelmintic and useful against intestinal worms, dyspepsia and skin diseases. The berries enter into the composition of several applications for ring-worms, itches and other skin diseases. The Hakims consider it to be attenuant and a purgative of phlegmatic humours; also a valuable anthelmintic specially against tape worms.

Embelia ribes is a large scandent shrub which grows throughout India, specially in the lower reaches of the Vindhya Hills. It bears, towards the end of autumn, abundant crops of smooth, nearly globular berries, $\frac{1}{4}$ inch in diameter, of an intense pink colour. These when collected and dried become shrivelled up with deep wrinkles all over the body and dark brown in colour. In this condition they are sold in the Indian bazzars.

Embelia ribes when extracted with various organic solvents, such as ether, benzene, ligroin, ethyl acetate, etc., yields mainly (*i*) a dark coloured aliphatic oil, and (*ii*) an orange-yellow crystalline substance which has been wrongly named "embelic acid." The name is erroneous as the substance is not an acid in the true sense of the term, because it does not contain any carboxyl group, though of course it yields several metallic derivatives like rottlerin (Dutt, *J. Chem. Soc.*, 1925, **127**, 2044; *J. Indian Chem. Soc.*, 1928, **5**, 21), carthamin (Kametaka and Perkin, *J. Chem. Soc.*, 1910, **97**, 1415) or plumbagin (Ray and Dutt, *J. Indian Chem. Soc.*, 1928, **5**, 419).

Hence it has been renamed " Embelin " by the present investigators which is more in accordance with its chemistry and with the usual conventions of systematic chemical nomenclature.

Embelin was first isolated by Warden (*Pharm. J.*, 1888, *iii*, **18**, 601; **19**, 305), who obtained it by extracting *Embelia ribes* with alcohol. He studied a few of its chemical and physical properties including solubility and formation of metallic derivatives. He also advanced the formula $C_9H_{14}O_2$ for the substance. Later on Hefftter and Feurstein (*Arch. Pharm.*, 1900, **238**, 15) also isolated embelin by extracting the ripe capsules of *Embelia ribes* with ether and they studied the dibenzoyl, dihydro- and anilino-derivatives in detail. They advanced the formula $C_{18}H_{28}O_4$ for embelin and showed that when oxidised with potassium permanganate it yields lauric and formic acids.

The above represents the work that has hitherto been done on embelin and the present investigation was undertaken in order to elucidate the constitution of the substance which is of great medicinal importance. In the light of a natural organic colouring matter of unknown constitution, it also possesses considerable interest since it has been found by the present investigators to yield beautiful shades on wool and silk from alcoholic solution and to give various deeply coloured lakes with different metallic salts and hydroxides. In the latter respect embelin behaves as a polygenetic dyestuff like alizarin or purpurin.

The best method of extracting embelin from *Embelia ribes*, that has been found up to this time, is to extract the well dried and powdered berries with benzene, and ther crystallise the substance from xylene or solvent naphtha. In this process a considerable quantity of a dark coloured aliphatic oil is also extracted along with embelin from which the latter is separated completely during the crystallisation process. The aliphatic oil which yields a soap with caustic soda, seems to be of the same type as linseed or rape oil and is receiving further attention.

Embelin is an aliphatic or more probably an alicyclic or hydroaromatic compound, since it contains a high percentage of hydrogen and burns with a non-sooty flame. Its empirical formula is $C_9H_{14}O_2$, but the molecular weight by the cryoscopic method in benzene as well as the fact that it yields *iso*lauric acid on oxidation shows that the formula must be doubled in order to get the molecular formula, which consequently becomes $C_{18}H_{28}O_4$. Molecular

weight determinations of the substance from the silver and lead salts also point to the same conclusion.

Embelin contains two highly reactive hydroxyl groups. This is shown by the formation of various metallic compounds of embelin containing two equivalents of metal, as well as by the formation of a diacetyl, a dibenzoyl, a dicarbethoxy, and a dimethyl derivative. Embelin also contains two ketonic groups as is shown by the formation of a dioxime, a disemicarbazone, a dihydrazone and a diphenylhydrazone. On account of the same reason, it also reacts with various primary amines such as methylamine, ethylamine, aniline *o*-toluidine, etc., with elimination of two molecules of water and formation of the corresponding amino-derivative. These amino-compounds are easily hydrolysed by boiling concentrated hydrochloric acid regenerating embelin. The latter, however, does not react with secondary amines under any conditions. The formation of a tetra-oxime of embelin shows that the two hydroxy-groups present in the molecule are capable of keto-enol tautomerism under suitable conditions. Further evidence of this fact by the formation of a dibenzoyldioxime, dianilinodioxime, a dibenzoyldisemicarbazone and a dianilinodisemicarbazone. It is also interesting to note that dianilinoembelin dioxime for example can be prepared by the action of aniline on embelin dioxime as well as by the action of hydroxylamine on dianilinoembelin. Similar is the case with the three other derivatives mentioned above.

Oxidising agents act on embelin with the greatest ease and the molecule is broken into smaller fragments amongst which *iso*lauric acid and oxalic acid have been definitely isolated and identified. Fuming nitric acid also brings about the same transformation. The present authors could not isolate any *n*-lauric or formic acid as obtained by Heffter and Feuerstein (*loc. cit.*). The lauric acid that they have isolated does not correspond in properties to the *n*-lauric acid which has been described in great detail by Oudemans (*J. Chem. Soc.*, 1863, **16,** 331), who has also described no less than twelve metallic salts of the acid. Hence the acid is really *iso*lauric acid and this is confirmed by the fact that on further oxidation with potassium permanganate it yields *iso*caproic acid.

On bromination embelin yields a tetrabromo-derivative with evolution of hydrogen bromide. The bromo-compound thus formed is easily decomposed by concentrated alkali into smaller fragments, the nature of which is at present under investigation.

Experimental.

The ripe capsules of *Embelia ribes* were carefully dried in the sun and then ground to a fine powder in a grinding machine. One kg. of the powder at a time was repeatedly extracted with benzene until the last extract was almost colourless. The combined extracts after filtration were distilled from a water-bath until benzene ceased to come over in the distillate. The residue on being poured out into a large shallow basin and allowed to stand overnight, solidified to masses of minute yellow glistening crystals embedded in a viscous brown mother-liquor. The latter was removed by extracting the mass with cold xylene and the residue crystallised from hot xylene or solvent naphtha in fine golden spangles with metallic lustre. It also crystallises from alcohol or ligroin in long yellow needles containing the corresponding solvent of crystallisation. But these fall to a fine yellow powder on drying in the steam-oven. It melts at 142°.

Embelin is fairly soluble in most of the organic solvents, but insoluble in water. It dissolves in dilute caustic alkalis yielding greyish-violet solutions which are easily oxidised in presence of air. In alcoholic solution embelin yields, with neutral ferric chloride, a dark reddish-brown, with silver nitrate a greyish-brown, with copper acetate, a brownish green, and with lead acetate, a dark green precipitate. On heating on a platinum foil, embelin first melts, then swells up and chars and then burns completely with a yellow non-sooty flame. It gives a dark red coloration with concentrated sulphuric acid. [Found: C, 69·73; 69·91; H, 8·9; 9·2. $C_{18}H_{28}O_4$ requires C, 70·13; H, 9·09 per cent. M. W. (1) (cryoscopic method in benzene)=304, (2) by lead salt *=298, (3) by silver salt*=310. Calc. M. W.=308.].

Diacetylembelin.—All ordinary methods of acetylation having failed to produce a crystalline derivative, the following modified method was adopted with success: Embelin was converted into the corresponding lead salt by treatment with lead acetate in alcoholic solution. The crystalline lead salt was filtered off and thoroughly washed with hot alcohol until free from soluble lead. It was then carefully dried, suspended in dry benzene and treated with a slight excess of acetyl chloride. The mixture was refluxed on the water-bath for 15 minutes and then filtered from the lead

* Taking embelin to be dibasic.

chloride that had separated out. The filtrate on evaporation to dryness yielded the diacetyl derivative as a yellow crystalline mass which was recrystallised from dilute alcohol in fine, long, yellow needles with silky lustres, m. p. 54°. (Found: C, 66·9 ; H, 7·9. $C_{18}H_{26}O_2.(O{\cdot}CO{\cdot}CH_3)_2$ requires C, 67·3 ; H, 8·19 per cent.).

Dibenzoylembelin.—Embelin (5 g.) was dissolved in 30 c. c. of pyridine in the cold and benzoyl chloride (10 c. c.) gradually added with vigorous shaking and cooling at the same time. The mixture was then warmed on the water-bath for 10 minutes and poured into dilute hydrochloric acid. A light brown oil separated out which on stirring immediately solidified. This was crystallised from alcohol with the addition of animal charcoal in colourless glistening needles melting at 97-98°. (Found: C, 74·2 ; H, 6·98. $C_{18}H_{26}O_2{\cdot}(O{\cdot}CO{\cdot}C_6H_5)_2$ requires C, 74·4 ; H. 7·0 per cent.).

Dicarbethoxyembelin.—Embelin (5 g.) dissolved in pyridine (30 c. c.) was treated with ethyl chlorocarbonate (10 g.) in the cold and the mixture warmed on the water-bath for half an hour. On pouring into dilute hydrochloric acid, the carbethoxy-compound seprated in flocks, which were filtered off and crystallised from dilute acetic acid and then from benzene in fine, colourless needles melting with decomposition at 266°. The substance is very easily hydrolysed with regeneration of embelin by the action of dilute caustic alkalis. (Found: C, 63·3 ; H, 7·6. $C_{18}H_{26}O_2{\cdot}(O{\cdot}CO{\cdot}OC_2H_5)_2$ requires C, 63·7 ; H, 7·9 per cent.)

Embelin Dimethyl Ether.—The silver salt of embelin (5 g.) suspended in absolute methyl alcohol (50 c. c.) was refluxed on the water-bath for two hours with methyl iodide (10 g.). The precipitated silver iodide was filtered off and the filtrate evaporated when a brown oil was obtained. This did not solidify even on standing at the ordinary temperature for a month. But on cooling in a freezing mixture it solidified to a crystalline mass, which melted again on reaching the ordinary temperature. It could not be distilled without decomposition even at 0·5 mm. In spite of repeated attempts at purification, the substance could not be obtained sufficiently pure for analysis.

Dianilinoembelin.—A mixture of embelin (5 g.) and freshly distilled aniline (12 g.) was gently boiled under reflux for 15 minutes and then poured into excess of dilute hydrochloric acid. The dark coloured precipitate was filtered off, washed thoroughly with dilute hydrochloric acid and water, dried and crystallised from pyridine in

dark violet leaflets with silky lustre, m. p. 167-68°. The substance is easily hydrolysed by boiling with concentrated hydrochloric acid with regeneration of embelin. (Found: N, 6·3. $C_{18}H_{28}O_2.(N{\cdot}C_6H_5)_2$ requires N, 6·1 per cent.).

Di-o-toluidinoembelin.—This compound was prepared from embelin and *o*-toluidine in a similar manner. It crystallises from pyridine in fine, bronze leaflets melting at 144-145°. (Found: N, 6·04. $C_{18}H_{28}O_2{\cdot}(N{\cdot}C_6H_4{\cdot}CH_3)_2$ requires N, 5·8 per cent.)

Dimethylaminoembelin.—Finely powdered embelin (5 g.) was digested with excess of 33% methyl alcoholic solution of methylamine on the water-bath under reflux for two hours. The mixture was then acidified and the precipitate filtered off and washed with water. It was then crystallised from alcohol in glistening blue needles with a coppery reflex, m. p. 216°. (Found: N, 8·57. $C_{18}H_{28}O_2{\cdot}(NCH_3)_2$ requires N, 8·38 per cent.).

Diethylaminoembelin.—This was prepared from embelin and ethylamine (33% sol.) in a manner similar to the above. It crystallised from alcohol in dark green needles with silky lustre, m. p. 212°. (Found: N, 8·1. $C_{18}H_{28}O_2{\cdot}(N{\cdot}C_2H_5)_2$ requires N, 7·7 per cent.)

Embelin Dioxime.—A mixture of embelin (5 g.), hydroxylamine hydrochloride (4 g.) and pyridine (30 c. c.) was heated on a boiling water-bath for one honr. It was then poured into dilute hydrochloric acid when a pale yellow compound separated out. This was filtered off, washed with water and crystallised from acetic acid in pale yellow needles melting at 278°. The substance is soluble in most of the organic solvents and also in caustic alkalis with an intense yellow colour. Alcoholic solutions of the substance yield, with ferric chloride—a reddish-brown, with lead acetate—a bright yellow, with copper acetate—a dark green and with silver nitrate—a buff coloured precipitate. The substance can be reconverted to embelin by boiling with concentrated hydrochloric acid. (Found: N, 8·1. $C_{18}H_{28}O_2{\cdot}(NOH)_2$ requires N, 8·2 per cent.).

Embelin Tetraoxime.—A mixture of embelin (5 g.), hydroxylamine hydrochloride (6 g.), sodium acetate (5 g.) and 70% alcohol (100 c. c.) was refluxed on the water-bath for three hours. The alcohol was then distilled off from the water-bath as far as possible and the residue poured into dilute hydrochloric acid. The resultant white precipitate was filtered off, washed with water and crystallised from dilute alcohol in colourless needles melting at 175°. The substance can be prepared from the dioxime by further treatment with hydroxylamine.

The tetraoxime is more soluble than the dioxime in the ordinary organic solvents. It dissolves in caustic alkalis with an intense orange-yellow colour, and its alcoholic solutions yield precipitates with ferric chloride, lead acetate, copper acetate and silver nitrate, the colours of which are more intense than the corresponding derivatives of the dioxime. (Found: N, 15·6. $C_{18}H_{28}(N{\cdot}OH)_4$ requires N, 15·2 per cent.)

Embelin Diphenylhydrazone.—Embelin (5 g.) and phenylhydrazine (6 g.) in glacial acetic acid (50 c. c.) were heated on the water-bath for an hour when the whole of embelin went into solution and the latter became dark red in colour. It was then poured into water. The resultant brick-red precipitate was filtered off, washed with water and crystallised from alcohol in brownish-red needles melting at 189-190° with decomposition. (Found: N, 10·98. $C_{18}H_{28}O_2{\cdot}(N{\cdot}NH{\cdot}C_6H_5)_2$ requires N, 11·4 per cent.).

Embelin Disemicarbazone.—A mixture of embelin (5 g.), semicarbazide hydrochloride (6 g.), sodium acetate (5 g.) and alcohol (70%, 100 c. c.) was heated on the water-bath under reflux for two hours. The mixture was then poured into water when the semicarbazone separated in brown flocks which were filtered off, washed with water and crystallised from dilute alcohol with the addition of animal charcoal in pale brown needles melting at 236° with decomposition. (Found: N, 19·7. $C_{18}H_{28}O_2{\cdot}(N{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$ requires N, 19·9 per cent.).

Embelin Dihydrazone.—Embelin (3 g.) dissolved in alcohol (50 c. c.) was treated with a slight excess of hydrazine hydrate (1·6 g. of 50%) in the cold and the mixture warmed on the water-bath for 10 minutes. On pouring into dilute hydrochloric acid, a yellow compound separated out which was filtered off and crystallised from pyridine in fine yellow needles melting at 204-205°. (Found: N, 16·7. $C_{18}H_{28}O_2{\cdot}(N{\cdot}NH_2)_2$ requires N, 16·6 per cent.).

Dianilinoembelin Dioxime.—Dianilinoembelin (2 g.) dissolved in pyridine (40 c. c.) was treated with hydroxylamine hydrochloride (1·5 g.) and the mixture heated on a boiling water-bath for one hour. On pouring into dilute hydrochloric acid, a light brown crystalline crust separated out which was recrystallised from alcohol in fine, brownish-white, prismatic needles melting at 162° with decomposition. The substance can also be prepared by the action of aniline on embelin dioxime. It can be reconverted to embelin by boiling with concentrated hydrochloric acid. The substance is sparingly

soluble in most of the organic solvents and insoluble in water. It dissolves in caustic alkalis with a dark brown colour. (Found: N, 11·1. $C_{18}H_{28}\cdot(N\cdot OH)_2\cdot(NC_6H_5)_2$ requires N, 11·5 per cent.)

Dianilinoembelin Disemicarbazone.—This compound was prepared from dianilinoembelin and semicarbazide hydrochloride in a similar manner. It crystallises from pyridine in fine, brown, microscopic needles melting at 145° with decomposition. (Found: N, 19·7. $C_{18}H_{28}\cdot(NC_6H_5)_2\cdot(N\cdot NH\cdot CO\cdot NH_2)_2$ requires N, 19·58 per cent.).

Dibenzoylembelin Dioxime.—A mixture of dibenzoylembelin (5 g.), hydroxylamine hydrochloride (2 g.), absolute alcohol (100 c. c.) and alcoholic caustic soda (10 c. c., 12%) was heated on the water-bath under reflux for two hours. On pouring into dilute hydrochloric acid, a crystalline mass was obtained which was filtered off, washed and recrystallised from acetone in colourless needles melting at 139°. The substance is sparingly soluble in most of the organic solvents, but dissolves in dilute caustic alkalis with a bright yellow colour. (Found: N, 5·1. $C_{18}H_{26}\cdot(O.CO\cdot C_6H_5)_2\cdot(N\cdot OH)_2$ requires N, 5·1 per cent.).

Dibenzoylembelin Disemicarbazone.—This was prepared from dibenzoylembelin and semicarbazide hydrochloride. It crystallised from absolute alcohol in short, brown prisms melting at 221° (decom.) (Found: N, 13·7. $C_{18}H_{28}\cdot(O.CO\cdot C_6H_5)_2\cdot(N\cdot NH\cdot CO\cdot NH_2)_2$ requires N, 13·3 per cent.).

Dibenzoylembelin Dianilide.—A mixture of dibenzoylembelin (5 g.) and freshly distilled aniline (15 c. c.) was heated in a distilling flask immersed in an oil-bath at 150°, until no more water was given off (about 1½ hours). The mixture was then cooled and poured into dilute hydrochloric acid when a voluminous brown precipitate separated out. This was filtered off, washed, dried and crystallised first from xylene and then from pyridine in clusters of dark brownish-red needles with beetle-green iridescence and metallic lustre, m. p. 176°.

The substance is practically insoluble in most of the organic solvents, with the exception of nitrobenzene, xylene, aniline, phenol and pyridine, in which it dissolves only to a small extent. It gives an intense violet colour with concentrated sulphuric acid. The substance can also be prepared by the action of benzoyl chloride on dianilinoembelin in pyridine solution. (Found: N, 4·6. $C_{18}H_{26}\cdot(O\cdot CO\cdot C_6H_5)_2\cdot(N\cdot C_6H_5)_2$ requires N, 4·2 per cent.).

Tetraacetyldihydroembelin.—Embelin (5 g.) dissolved in boiling acetic anhydride (50 c.c.) was gradually treated with moist zinc dust (7 g.) until the solution was completely decolorised. On pouring into water and stirring for some time the tetra-acetyl derivative separated as a colourless mass which was filtered off and recrystallised from dilute alcohol in colourless, long needles with silky lustre, m. p. 124°.

The substance is freely soluble in most of the organic solvents but insoluble in water. It is very easily hydrolysed by boiling with dilute acids and alkalis, yielding dihydroembelin as an intermediate product, which very quickly gets oxidised to embelin in presence of air, specially in alkaline solution. (Found: C, 65·0; H, 7·6. $C_{18}H_{26}\cdot(O\cdot CO\cdot CH_3)_4$ requires C, 65·27; H, 7·9 per cent.).

Dihydroembelin.—The above tetra-acetyl derivative (5 g.) was dissolved in absolute alcohol (100 c.c.) containing 15 c.c. of conc. sulphuric acid, and the solution warmed on the water-bath for 15 minutes. A pinch of zinc dust was added to completely decolorise the solution which was then quickly filtered and diluted to 500 c. c. with boiled distilled water. The opalescent solution was allowed to stand overnight in a tightly corked flask, when large glistening leaflets with fatty lustre were obtained. These were then recrystallised from dilute alcohol containing sulphurous acid, m. p. 117°. The substance is identical with the dihydroembelic acid of Heffter and Feurstein (*loc. cit.*).

The substance is soluble in all the organic solvents and also to a slight extent in water yielding solutions which oxidise rapidly in air specially in presence of a trace of alkali. In alcoholic solution, with neutral ferric chloride it produces a dark reddish-brown, with copper acetate—a greenish-brown, with silver nitrate—a greyish-white and with lead acetate—an olive green precipitates. In perfectly dry condition the substance is, however, quite stable in the air. (Found: C, 69·7; H, 9·9. $C_{18}H_{30}O_4$ requires C, 69·67; H, 9·67 per cent.).

Tetrabromoembelin.—Embelin (5 g.) dissolved in carbon tetrachloride (250 c.c.) was treated with excess of bromine (12 g.) dissolved in the same solvent. The mixture was allowed to stand at the ordinary temperature for about 24 hours and then warmed on the water-bath for three hours. The excess of bromine and carbon tetrachloride were distilled off and the residual heavy liquid washed several times with a mixture of aqueous potassium iodide and sodium thiosulphate, and then with water. The resultant product, on allowing to stand for about two days, solidified to a colourless

crystalline mass which was recrystallised from alcohol in colourless glistening prisms melting at 132°. The substance is fairly soluble in most of the organic solvents as well as in dilute caustic alkalis. In strong alkaline solutions, however, it decomposes very quickly. (Found: Br, 51·6. $C_{18}H_{24}O_4Br_4$ requires Br, 51·28 per cent.).

Action of Fuming Nitric Acid.—Embelin (5 g.) was treated with fuming nitric acid (30 c.c. *d* 1·51) in the cold and the dark red solution warmed on the water-bath for half an hour. On pouring into water an oil separated which was extracted with chloroform. The chloroform solution was washed with water, dried and the chloroform evaporated, when a thick colourless oil was obtained which solidified on long standing into a crystalline mass melting at 33-35°. It was found to be an aliphatic monocarboxylic acid with a molecular weight of 202 (by silver salt method) and was identified to be *iso*lauric acid. On further oxidation with potassium permanganate it gave *iso*caproic acid.

Oxidation of Embelin with Potassium Permanganate.—Embelin (5 g.) dissolved in dilute sodium hydroxide was treated with a 3% solution of potassium permanganate at the ordinary temperature until the colour of permanganate was no longer discharged. A current of sulphur dioxide was then led through the mixture until the precipitated manganese dioxide had completely dissolved. The clear solution was then extracted with chloroform and from the chloroform solution *iso*lauric acid was definitely isolated and identified. The mother-liquor was found to contain oxalic acid, which was isolated and identified *via* the calcium salt. No other acid could be detected.

Further work in this direction is in progress.

Two of us (R. K., and A. C. R.) wish to express our indebtedness to the Kanta Prasad Trust of the Allahabad University for two research scholarships which enabled us to take part in the investigation.

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Preparation of Jellies of some Inorganic Substances.

By Satya Prakash and N. R. Dhar.

In previous publications (*Z. anorg. Chem.*, 1926, **152**, 399; 1927, **164**, 63; 1927, **168**, 209) we have studied the conditions of the formation of jellies of vanadium pentoxide, ceric hydroxide and hydroxides of zirconium, ferric iron, aluminium and chromium.

In this paper, we have investigated the conditions of the formation of following jellies, which we are the first to obtain:

(*i*) Ferric borate.
(*ii*) Ferric molybdate.
(*iii*) Ferric tungstate.
(*iv*) Thorium arsenate.
(*v*) Thorium phosphate.
(*vi*) Thorium molybdate.
(*vii*) Stannic arsenate.
(*viii*) Stannic phosphate.
(*ix*) Stannic tungstate.
(*x*) Stannic molybdate.
(*xi*) Stannic borate.

Jelly formation with ferric, zinc, cadmium, copper and manganese arsenates has been reported by Grimaux (*Compt. rend.*, 1884, **98**, 1540), Coloriano (*Bull. Soc. Chim. France*, 1886, **45**, 711), Deiss (*Kolloid Z.*, 1914, **14**, 139), Holmes and co-workers (*J. Amer. Chem. Soc.*, 1916, **38**, 1970; 1918, **40**, 1014; 1919, **41**, 763), Klemp and Gyulay (*Kolloid Z.*, 1918, **22**, 57; 1921, **28**, 262), Kraemer (*Colloid Symposium, Wisc.*, 1923, **1**, 61), Weiser (*ibid.*, 1923, **1**, 38) and others. No work seems to have been done before with jellies of borates, tungstates and molybdates.

Ferric molybdate jellies.

When potassium molybdate solution is added to a ferric chloride solution, a yellowish white precipitate is obtained, which dissolves on shaking, if ferric chloride is in excess. This clear mixture on standing for some time develops opalescence and finally, if concentrations are favourable, the whole mixture sets to a firm opaque jelly.

For preparation of these jellies 4 c.c. of $M/2{\cdot}69$-ferric chloride solution were taken in test tubes and varying amounts of 10% potassium molybdate solution were added, and the total volume in each case was made up to 10 c.c. by adding the requisite amount of water. The test tubes were well shaken after mixing the contents till clear solutions were obtained and then allowed to stand.

TABLE I.

Total volume = 10 c.c.

Ferric chloride.	Potassium molybdate, 10%.	Observations.
2 c.c.	1·5 c.c.	Solution becomes turbid but no jelly.
2	2·0	" " " "
2	2·5	Loose opaque jelly in 2 days with supernatant liquid.
2	3·0	Loose opaque jelly in 2 days with supernatant liquid.
1	3	No jelly.
4	3·5	Firm opaque jelly in 2 days.
4	4	Firm opaque jelly in a day.
4	5	Firm opaque jelly in a day.
5	5	Firm opaque jelly in a day.

Ferric borate jellies.

When a saturated solution of borax is added gradually to ferric chloride solution, a bulky precipitate occurs which goes on dissolving on shaking, but when sufficient quantity of borax has been added, the ferric borate settles down suddenly in the form of a bulky opaque jelly, which begins to synerise soon, and then it breaks up.

We have also obtained transparent ferric borate jelly by dialysing a mixture of 60 c.c. of ferric chloride ($M/2{\cdot}69$) and 45 c.c. of 20% borax containing an excess of ferric chloride to peptise ferric borate. The clear red solution was allowed to dialyse for 30 days. The red sol thus obtained sets to a fine transparent red jelly on addition of potassium chloride or potassium sulphate.

TABLE II.

Concentration of the sol=11·78 gm. ferric borate per litre.

Electrolyte. (c.c.)	Ferric borate. (c.c.)	Total volume. (c.c.)	Observation.
N-KCl 0·3	3·0	3·3	Instantaneously clear red gel; syneresis begins within 5 minutes.
N-KCl 0.2	3·0	3·2	Instantaneously clear red gel; synerises soon.
N-KCl 0·4	3	3·4	Instantaneously sets up but immediately breaks up.
N-KI 0·1	3·0	3·1	,, ,, ,,
N/10-KCl 0·3	3·0	3·3	Transparent gel in 2 minutes.
N/10-KCl 0·2	3·0	3·2	Transparent gel setting in 10 minutes; no syneresis.
N/10-KCl 0·1	3·0	3·1	Sets in 10 hours; no syneresis.
N-KCl 0·1	5·0	5·1	Instantly clear gel.
N/10-KCl 0.2	2·0	3·2	Transparent gel in 15 minutes; no syneresis in 2 days.
N/50-K_2SO_4 0·2	3·0	3·2	Transparent gel in 4 days; no syneresis in even 2 days.

In almost all the cases, syneresis soon begins: the greater the concentration of the electrolyte, the more rapid is the syneresis.

Thorium molybdate jelly.

When potassium molybdate solution is added to thorium nitrate, a white precipitate of thorium molybdate occurs, but if the mixture is vigorously shaken, this precipitate goes on dissolving till a clear viscous solution is obtained. On standing for some time, the whole mass sets to a transparent colourless jelly. These jellies are very stable and do not synerise and do not become turbid markedly on keeping for months.

5 C.c. of a solution of thorium nitrate containing 12·035 gm. in 250 c.c. were taken in test tubes and various amounts of 3% or 10% potassium molybdate were added and the solutions made up to 6 c.c. in each case. The mixtures were vigorously shaken for 5 minutes and the time for gelation was recorded.

TABLE III.

Total volume=6 c.c.

Thorium nitrate.	Potassium molybdate (3%).	Observation.
5 c.c.	1 c.c.	Transparent jelly in 5 hours with slight opalescence; stable.
5	0·8	Transparent jelly in 5½ hours.
5	0·6	Transparent jelly in 24 hours.
5	0·4	No jelly in a week.
5	0·2	,, ,, ,,
5	0·5 (of 10 %)	Transparent jelly in 1 hour 8 mins.
5	1·0 (of 10 %)	Opaque jelley in 40 minutes, but breaks up in 12 days.
3	1	Transparent jelly within 22 hours, breaks up in 12 days.
3	0·6	Transparent jelly within 22 hours.

Thorium phosphate jellies.

No phosphate jellies have been prepared before without dialysis, by directly mixing the constituents of the reaction. Thorium phosphate jellies, which we have obtained, are prepared with the same ease as zinc and manganese arsenate jellies and these are perfectly transparent, firm and colourless and are very stable. Time of gelation can be extended to a very long period by varying the concentrations. The time of gelation in the cases of manganese and zinc arsenate jellies, however, could not be extended beyond 10-15 minutes.

5 C.c. of a solution of thorium nitrate (12·035 gm. in 250 c.c.) were taken in test tubes and varying amounts of potassium phosphate (22% solution) were added, keeping the total volume in all cases to 6 c.c. The mixtures were well shaken for 3 minutes and then allowed to stand. The nature of jelly and period of gelation were recorded.

TABLE IV.

Total volume=6 c.c.

Thorium nitrate.	Potassium phosphate (22 %).	Observation.
5 c.c	1 c.c.	Transparent jelly after 22 hours.
5	0·7	Transparent jelly after 78 hours.
5	0·5	Instantaneously white opaque jelly.
5	0·3	Transparent jelly in 15 minutes.
5	0·2	Transparent jelly in 4 hours.
3	0·3	Precipitated to a opaque jelly with supernatant liquid in 2 hours.
3	0·7	Transparent jelly after 22 hours.

Thorium arsenate jellies.

These jellies resemble manganese and zinc arsenate jellies in their mode of preparation but differ from them in being slightly turbid, and also in the fact that these require much higher concentration of arsenate solution for preparation. When to thorium nitrate solution a few drops of potassium arsenate solution are added, gelatinous precipitate appears which dissolves on shaking and finally the whole mass sets to a firm jelly. These arsenate jellies are either translucent or opaque and their opacity increases with time on standing. A slight syneresis appears to begin just after their formation but it does not proceed far. These jellies are quite stable and hard.

5 C.c. of a solution of thorium nitrate (12·035 gm. in 250 c.c.) were taken in test tubes and various amounts of potassium arsenate (45 gm. in 250 c.c) solution were added to it and the mixture was shaken for 2 minutes. The total volume in each case was kept to be 6 c.c.

TABLE V.

Total volume = 6 c.c.

Thorium nitrate.	Potassium arsenate.	Observation.
5 c.c.	0·25 c.c.	Translucent jelly after 22 hours.
5	0·30	Translucent jelly in 1 hour.
5	0·40	Translucent jelly in 5 minutes.
5	0·50	Translucent jelly in 1 minute; a slight syneresis soon begins.
5	1·0	Instantaneously, white opaque jelly.
5	0·15	No jelly but white precipitate in 10 days.
3	0·4	Translucent jelly setting in 1 minute.
3	0·3	Translucent jelly in 45 minutes.

Stannic arsenate jellies.

Stannic chloride solution, when mixed with potassium arsenate solution, gives the precipitate of stannic arsenate ; but if stannic chloride be in excess, this precipitate dissolves and a clear colourless solution is obtained. In these solutions, opalescence begins within five minutes and finally stable jellies are obtained provided the concentrations are favourable. These jellies are almost transparent with very slight opalescence in the beginning when freshly formed, but opacity increases with time and finally they become white and opaque. Opacity also increases with the concentration of potassium arsenate solution used.

To 2 or 3 c.c. of $M/1{\cdot}099$-stannic chloride solution, varying concentrations of potassium arsenate solution (45 gm. in 250 c.c.) are mixed and the volume is kept constant. The following are the observations when jellies were allowed to set at the room temperature (18-20°).

TABLE VI.

Total volume = 6 c.c.

Stannic chloride.	Potassium arsenate.	Observation.
3 c.c.	3 c.c.	Transparent jelly in 25 minutes ; becomes opalescent and finally opaque.
3	2	Sets to a transparent jelly in 1½ hour.
3	1	Opaque jelly within 23 hours.
2	4	Sets to opaque white firm jelly in 2 minutes.
2	3	Sets to translucent jelly in 5 minutes.
2	2	Sets to translucent jelly in 6 minutes.
2	0·5	Sets to opaque jelly in 24 hours.
1	1·0	Sets to translucent jelly in 2 minutes.

It has been observed that greater the concentration of stannic chloride, the more will be the transparency of the freshly formed jelly. Undoubtedly all jellies become equally opaque on standing for a long time.

The process of gelation is greatly accelerated by raising the temperature, though the jellies formed at higher temperatures are more opaque and perhaps less fine in texture. The results recorded in the

following table are of the same jellies of same concentration as the above except that these have been warmed for 5 minutes in a bath of constant temperature of 90°.

TABLE VII.

Total volume=6 c.c.

Stannic chloride.	Potassium arsenate.	Observation.
3 c.c.	3 c.c.	Sets in 3 minutes to opaque jelly.
3	2	Sets in 6 minutes to opaque jelly.
3	1	Sets in 10 hours to opaque jelly.
3	0·5	Highly viscous liquid but does not set even in 10 days.
2·0	0·5	Sets to loose opaque jelly in 5 minutes.

Stannic phosphate jelly.

Stannic phosphate jelly has been obtained in the same way as stannic arsenate. When potassium phosphate (KH_2PO_4) is added to stannic chloride solution, stannic phosphate is precipitated and under favourable concentrations, even transparent jellies are obtained which are mostly accompanied with very slight opalescence. The jellies, however, become quite opaque within a few hours after setting. 3 C.c. of stannic chloride ($M/1·099$) solution were taken in test tubes and various amounts of potassium phosphate solutions (55 gm. in 250 c.c.) were added, and the total volume was made up to 6 c.c. in every case.

TABLE VIII.

Total volume=6 c.c.

Stannic chloride.	Potassium phosphate.	Observation.
3 c.c.	3 c.c.	Sets in 15 minutes to translucent firm jelly.
3	2	Sets in 18 minutes to translucent firm jelly.
3	1·5	Sets in 30 minutes to ,, ,,
3	1·0	Sets in 2 hours ,, ,,
3	0·5	Sets to jelly in 22 hours.
2	2	Sets in 4 minutes to opaque jelly.
2	1	Sets to transparent jelly in 7 minutes.
1	0·5	Sets in 2 minutes to white opaque jelly.

All these jellies, though differ initially in their transparency, become opaque after keeping for a few days. These are very stable and hard and do not exhibit any marked syneresis. The speed of gelation is much accelerated by allowing them to set at higher temperatures. The following table records the observations taken at 90°. 3 C.c. of stannic chloride ($M/1{\cdot}099$) solution, mixed with various amounts of potassium phosphate solution, were warmed in a bath of constant temperature at 90°, and the time of setting was noted. All jellies formed at this temperature are mostly opaque from the beginning of formation and are quite stable and hard and do not undergo any marked syneresis.

TABLE IX.

Total volume = 6 c.c.

Stannic chloride.	Potassium phosphate.	Observation.
3 c.c.	2 c.c.	Sets to translucent jelly in 1 minute.
3	1·5	Sets to opaque jelly in 2 minutes.
3	1·0	Sets to opaque jelly in 3 minutes.
3	0·5	Sets to opaque jelly in 5 minutes.

Stannic tungstate jellies.

We have also prepared stannic tungstate jellies. 1·5 or 2 c.c. of stannic chloride solution (1·53 *M*) were taken in test tubes and to them various amounts of 15% sodium tungstate solution were added and the total volume was always made up to 6 c.c. Each mixture was thoroughly shaken for 5 minutes, when a turbid solution was obtained. The solution became quite clear after keeping for another 10 minutes. After some period, which differs according to the concentration of sodium tungstate, slight opalescence begins which intensifies and finally an opaque jelly is obtained.

TABLE X.

Total volume = 6 c.c.

Stannic chloride.	Sodium tungstate.	Observation.
2 c.c.	2 c.c.	Opalescent solution, no jelly.
2	2·50	Opalescent solution, no jelly.
2	3	Sets to opaque firm jelly in 5 days.
2	3·5	Sets to opaque firm jelly in 2½ days.
2	4	Sets to opaque firm jelly in 12 hrs.
1·5	4	Sets to opaque firm jelly in 1½ hrs.
1·5	3·5	Sets to opaque firm jelly in 3 hrs.

All these jellies are opaque, white, hard and stable and do not undergo any marked syneresis. The gelation in this case is also accelerated if setting is done at a higher temperature. 2 C.c. of stannic chloride solution (1·53*M*) were mixed with various amounts of 15% sodium tungstate and the mixture was shaken for 5 minutes and then warmed in a bath at 93° till the contents set to jelly.

TABLE XI.

Total volume = 6 c.c.

Stannic chloride.	Sodium tungstate.	Observation.
2 c.c.	2 c.c.	Warmed for 20 minutes but no jelly; only white turbid solution obtained.
2	2·5	Sets in 20 minutes to white opaque jelly.
2	3·0	Sets in 8 minutes to opaque jelly.
2	3·5	Sets in 6 minutes to opaque jelly.
1·5	2	Sets in 8 minutes to opaque jelly.

A slight syneresis appears when jellies are transferred from the bath to room temperature (19°) but the syneresis does not proceed any further. Jellies prepared in the hot are also quite stable and hard.

Stannic borate jellies.

When a saturated borax solution obtained at 90° is added to 1·5 *M*-stannic chloride solution, a white precipitate of stannic borate is formed which dissolves on shaking. If suitable concentrations are chosen and the mixture is warmed at 90°–95°, loose white opaque jelly is obtained which breaks up in a short time. If stannic chloride solution contains much free hydrochloric acid, which is always associated with hydrated stannic chlorides, stannic borate does not set even on warming.

To 1·5*M*-stannic chloride solution, a saturated borax solution is added and the mixture containing an excess of stannic chloride was dialysed for 24 hours; a clear transparent sol was obtained, which sets to transparent jellies on addition of electrolytes like potassium chloride or sulphate. The sol itself becomes more and more viscous even without the addition of electrolytes and sets within 24 hours.

TABLE XII.

Concentration of sol = 66·40 gm. SnO_2 per litre.
Sol taken = 2 c.c. Total volume = 4 c.c.

Electrolyte.		
$N/15$-K_2SO_4	0·5 c.c.	Firm opaque jelly in half-minute.
	0·3	Translucent jelly in 2 minutes.
	0·1	Transparent jelly with slight opalescence in 5 minutes.
	0·05	Transparent jelly with slight opalescence in 7 minutes.
$N/5$-KCl	1·0	Transparent jelly in 6 minutes.
	0·5	Transparent jelly within 8 minutes.
	0·3	Transparent jelly in 10 minutes.
	0·1	Transparent jelly in 15 minutes.

These jellies are transparent at the time of formation, but opalescene soon develops and finally white and opaque jellies are formed. These jellies are quite firm and stable and do not show any marked syneresis.

Stannic molybdate jellies.

No jelly has been obtained by directly mixing the solutions of potassium molybdate and stannic chloride, whereby a white precipitate of gelatinous nature is only formed. However, if potassium molybdate (15% solution) be added below precipitation value to stannic chloride solution, and the mixture be allowed to dialyse for 24 hours, a clear sol with slight opalescence is obtained. The sol obtained contained 91·04 gm. of SnO_2 per litre. The sol is fairly stable and does not set to jelly without addition of electrolytes, but if it is half-diluted, it sets to a white translucent firm jelly within 6 hours. It appears to be stabilised in presence of potassium chloride though jellies are readily formed in presence of potassium sulphate, as is seen in the following table.

TABLE XIII.

Total volume = 4 c. c.

Tin molybdate sol.	Electrolyte,		
2 c.c.	$N/5$-K_2SO_4	1·5 c.c.	Translucent jellies in 6 hours.
2		1·0	White opaque jelly in 2 minutes.
2		0·5	White translucent jelly in 30 mins.
2		0·2	" " 75 "
2		0·1	Translucent jelly in 1½ hours.
2		0·5	" " 3 "
1		0·3	Loose opaque jelly in 5 minutes, syneresis soon begins.
1		0·1	Firm opaque jelly in 5 minutes.
1		0·05	" " 20 "
2	$N/1$-KCl	0·4	" " 40 "
2		1·0	Translucent jelly in 2 days.
2		2·0	" " "
			No jelly in 3 days.

Like other stannic jellies, these are almost transparent when freshly formed but become opaque on keeping for some time. Effect of temperature on formation of these jellies is also quite appreciable: the process of gelation appears to be accelerated by the rise in temperature. To 2 c.c. of the above sol, 2 c.c. of water are added and the time of gelation is noted at different temperatures.

TABLE XIV.

Temperature	90°	70°	60°	50°	40°	24°
Time of gelation (in mins.) ...	1	2	4	7	20	360

Transluscent jelly in all cases.

Ferric tungstate jellies.

When 15% solution of sodium tungstate is added to *M*/2-ferric chloride solution, a bulky precipitate is formed which dissolves to some extent on vigorous shaking but if the mixture is warmed in a water-bath at 96° for 5 minutes, it is completely dissolved and a clear transparent yellow solution is obtained, which sets to a fine yellow, opaque jelly when the concentrations are suitable.

TABLE XV.

The mixture has been warmed for 5 minutes at 95° in all cases. Total volume = 5 c.c.

M/2 Ferric chloride.	Sodium tungstate (15%).	
2 c.c.	3 c.c.	Yellow opaque jelly within 20 hours.
2	2·5	,, ,, ,,
2	2·0	Yellow opaque jelly in 2 days.
1·5	3·5	Bulky opaque yellow jelly in 3 minutes.
1·5	3·0	,, ,, 5 ,,
1·5	2·5	Fine opaque yellow jelly in 5 minutes.
1·5	2·0	,, ,, 2 days.
1·5	1·5	No jelly in 3 days.

These jellies resemble ferric molybdate jellies. Opaque, yellow ferric arsenate and phosphate jellies are also obtained if suitable amount of potassium arsenate or phosphate solutions are added to ferric chloride solutions. However, so long as ferric chloride is

much in excess to peptise ferric arsenate and phosphate, clear red sols are obtained which give beautiful transparent jellies on dialysis as prepared by Holmes and co-workers. In the case of tungstate and molybdate, no red sols are obtained on mixing ferric chloride and sodium tungstate or potassium molybdate and as such, on dialysis, these mixtures do not give transparent jellies.

Further work on jelly formation is in progress in these laboratories.

Summary.

The following inorganic jellies have been obtained for the first time and their method of preparation described :—

(1) Ferric borate, (2) ferric molybdate, (3) ferric tungstate, (4) thorium arsenate, (5) thorium phosphate, (6) thorium molybdate, (7) stannic arsenate, (8) stannic phosphate, (9) stannic tungstate, (10) stannic molybdate, and (11) stannic borate.

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On the Preparation of Dithiophosphates and some new Dithiophosphates.

By Panchanan Neogi and Munindra Chandra Ghosh.

Sodium monothiophosphate was first obtained by Wurtz (*Ann. chim. phys.*, 1847, *iii* **20**, 443) by the interaction of caustic soda and phosphorus thiochloride. Kubierschky (*J. pr. Chem.*, 1885, *ii*, **31**, 93) obtained several mono- and di-thiophosphates by the action of caustic soda on phosphorous pentasulphide. The solution thus obtained probably contained trithiophosphate as well, but it was not isolated. He, however, separated the three varieties of thiophosphates by variation in temperatures. We repeated his experiments but found it extremely difficult to obtain the thiophosphates in the pure condition. The mixture formed by the action of caustic soda on phosphorous pentasulphide was treated by Kubierschky with alcohol and the resultant oil was separated, dissolved in water and heated to 50°-55° to decompose the trithiophosphate and to 90° to decompose the dithiophosphate as well, leaving the monothiophosphate undecomposed. But our experience showed that heating the solution to a particular temperature failed to separate the three thiophosphates except with great difficulty. Kubierschky advised to heat the solution until the smell of sulphuretted hydrogen was no longer perceived. On heating the solution however, we found it to be blackened, and suphuretted hydrogen was evolved continuously even when heated for two or three days at the particular temperatures mentioned by him. The resultant crystals from such solutions were impure and were separated with great difficulty. There are no methods for preparing the several varieties of thiophosphates singly without the accompaniment of other varieties.

The method, which succeeded so far as dithiophosphates are concerned, was the interaction of powdered phosphorous pentasulphide on magnesium oxide suspended in ice-cold water (*vide* Experimental), the reaction being as follows:

$$3MgO + P_2S_5 + H_2O = Mg_3P_2S_4O_4 + H_2S.$$

The sodium salt was obtained by double decomposition with caustic soda. In the case of other soluble thiophosphates such

as those of potassium, ammonium and calcium the corresponding hydroxides were used in the place of caustic soda. Insoluble dithiophosphates were prepared by double decomposition of the sodium salt with soluble salts of different metals. By this method we have been able to prepare dithiophosphates of sodium potassium, calcium, ammonium, barium, magnesium, lead, thallium and zinc. The potassium, calcium, magnesium, lead, thallium and zinc compounds were hitherto unknown. Other dithiophosphates such as those of manganese, mercury (ic), thorium and lanthanum were also obtained, but they decomposed during drying. What were presumably dithiophosphates of bismuth, copper, mercury (ous), nickel, cobalt, cadmium, silver and ferrous iron were found to be still more unstable and decomposed within a few seconds of their precipitation. Their decomposition could be avoided for a few more seconds by the immediate addition of excess of alcohol, but even in the presence of alcohol their decomposition could not be prevented. It is to be understood that all operations including precipitations and filtrations were done in vessels containing ice and salt, washing being done with ice-water.

As regards the other varieties of thiophosphates, Kubierschky obtained the three varieties in the oil obtained by precipitation with alcohol. The oil or crystals obtained by our method did not contain either the mono- or tri-thiophosphates, so that this is a method of preparing dithiophosphates only.

Experimental.

Sodium Dithiophosphate, $Na_3PS_2O_2 + 11H_2O$.

Magnesia (30 g.) was suspended in water in a beaker surrounded with ice and salt, and finely powdered phosphorous pentasulphide (22 g.) was then added. The brisk action which followed was allowed to proceed for 2-3 hours in order to complete the reaction, the beaker being kept surrounded with ice all the while. The solution was then filtered off from the excess of the reagents in a metallic funnel containing ice-water and a clear yellowish solution was obtained. From this solution the magnesium was precipitated as the hydroxide by adding a cold solution of caustic soda in small quantities at a time, avoiding excess. The completion of the decomposition was ascertained by filtering off a small portion from time to time until with the addition of only a few drops of the caustic soda solution no further precipitate of magnesium hydroxide was noticed.

The whole of the magnesium hydroxide was now filtered off and to the clear filtrate an excess of cold alcohol was added. Very soon beautiful six-sided crystals were deposited and when the deposition was complete, the alcohol was decanted off and the crystals washed several times with alcohol in order to remove the impurities such as any adhering caustic soda and alkali sulphides. These were further purified by redissolving the crystals in water and reprecipitating with excess of alcohol. The crystals being washed with alcohol, rapidly became dry when pressed between filter papers. The salt responded to all the tests of dithiophosphates as given by Kubierschky of which the following are important and not given by other thiophosphates. A solution of sodium salt was used in all these tests.

(1) On the gradual addition of manganous sulphate solution, at first a green colouration was observed which on shaking turned darker and on further addition of the sulphate, gave a green precipitate which gradually became white. But this white precipitate on shaking changed its colour again and turned green.

(2) A solution of cobalt sulphate gave a green precipitate soluble in excess of sodium dithiophosphate to a green solution which rapidly became black owing to the formation of cobalt sulphide.

The dry salt was analysed and found to have the formula $Na_3PS_2O_2+11H_2O$, which agreed with Kubierschky's formula of the salt. The sulphur was oxidised to sulphate with concentrated nitric acid and bromine water and estimated as barium sulphate. The phosphate was estimated by dissolving the salt in concentrated hydrochloric acid, precipitating with magnesia mixture and estimating as pyrophosphate. (Found: S, 15·91 ; P, 8·63. $Na_3PS_2O_2$, $11H_2O$ requires S, 16·24 ; P, 7·86 per cent.). The sodium and other hydrated salts give out water when heated.

Potassium Dithiophosphate, $K_3PS_2O_2+4H_2O$.

Potassium dithiophosphate was obtained by Kubierschky in solution only. This compound, however, was obtained by us as a crystalline solid by the following method.

Phosphorus pentasulphide (15 g.) was allowed to react with magnesium oxide (21 g.) as previously described. The solution was filtered and caustic potash solution carefully added until the whole of magnesium was just precipitated as magnesium hydroxide. To the solution of the potassium salt thus obtained, an excess of alcohol

was added when an oil separated out. The alcohol was then decanted off and the oil washed several times with alcohol and collected. When kept in a vacuum desiccator over concentrated sulphuric acid inside an ice-chest containing a mixture of ice and salt, it formed a crystalline mass after three or four days. The crystals were rapidly dried between filter papers and analysed. When the oil was kept in a vacuum desiccator over sulphuric acid at the ordinary temperature, it underwent partial decomposition evolving sulphuretted hydrogen. The resulting solid contained very little dithiophosphate. It was not possible to separate the dithiophosphate from this mixture as an oil was again formed on treatment with alcohol. The pure dry salt could be kept undecomposed in an ordinary desiccator in an ice-chest only but slowly decomposed at the ordinary temperature. (Found: S, 20·55; P, 8·91. $K_3PS_2O_2+4H_2O$ requires S, 20·25; P, 9·81 per cent.).*

Ammonium Dithiophosphate, $(NH_4)_3PS_2O_2+2H_2O$.

The ammonium salt had been obtained by Kubierschky. It was obtained by our method also, substituting caustic soda by ammonium hydroxide. (Found: S, 30·06. $(NH_4)_3PS_2O_2+2H_2O$ requires S, 29·49 per cent.).

Magnesium Dithiophosphate, $Mg_3P_2S_4O_4+\text{-}H_2O$.

Magnesium dithiophosphate was obtained by Kubierschky who reported it to be soluble and unstable. No analysis was given and its formula was not established. The magnesium compound as prepared by us was a solid.

Powdered phosphorus pentasulphide (17 g.) was allowed to react with magnesium oxide (23 g.) in the usual manner. When the reaction subsided, the mixture was filtered off and to the filtrate an excess of alcohol was added when the magnesium salt was precipitated. It was washed with alcohol, redissolved in water and reprecipitated with alcohol. The salt was found to be very unstable so much so, that it could not be dried under an electric fan at the ordinary temperature. The salt was dried by keeping overnight in a vacuum desiccator in an ice-chest. It was found to have become

* The error in P is high owing to the small percentage of P. only. Better analytical results are hardly to be expected with such unstable compounds.

partly insoluble in water. (Found: S, 35·56. $Mg_3P_2S_4O_4+2H_2O$ requires S, 35·35 per cent.). Owing to the fact that it becomes partly insoluble on reprecipitation, the formula assigned to it here is doubtful.

Calcium Dithiophosphate, $Ca_3P_2S_4O_4+H_2O$.

The calcium was reported by Kubierschky to be soluble in water and unstable. He could not obtain it pure.

Powdered phosphorus pentasulphide (21 g.) was allowed to act upon magnesia (24 g.) in the usual way. To this solution cold lime water was carefully added avoiding any excess when magnesium hydroxide was precipitated, and the calcium dithiophosphate remaining in solution. The solution was filtered and the calcium salt precipitated with alcohol and purified as in previous cases. The salt being very unstable was dried in the same manner as the magnesium salt. For analysis, a weighed quantity of the salt was dissolved in concentrated nitric acid and the precipitation being completed in excess of absolute alcohol, the sulphate precipitated as $CaSO_4$. This was washed with 70% alcohol. The salt was found to be insoluble in alcohol. (Found: S, 32·03. $Ca_3P_2S_4O_4+H_2O$ requires S, 32·65 per cent.).

Barium Dithiophosphate. $Ba_3P_2S_4O_4+10H_2O$.

To a solution of the sodium salt, barium chloride solution was added when barium dithiophosphate was precipitated. The barium salt was washed with alcohol and dried between filter papers and then under an electric fan. The salt was comparatively stable and insoluble in water and alcohol.

The analysis was done as indicated before ; in this case however, part of the sulphur was precipitated out as barium sulphate during oxidation of the salt with concentrated nitric acid and bromine water. The excess of the sulphuric acid was then precipitated by the addition of barium chloride solution. The combined precipitate of barium sulphate was then washed, dried and weighed as usual. (Found: S, 14·81. $Ba_3P_2S_4O_4+10H_2O$ requires S, 15·14 per cent.).

Zinc Dithiophosphate, $Zn_3P_2S_4O_4+H_2O$.

To a solution of the sodium salt, zinc acetate* solution was added when the zinc thiophosphate was obtained as a white precipitate.

* Zinc sulphate solution, being acidic, was not suitable for precipitation, as in the acid solution the thiophosphate underwent decomposition.

It was washed with alcohol, and dried in a vacuum desiccator kept in an ice-chest containing ice and salt. It was a white powder, insoluble both in water and alcohol. (Found: S, 27·29. $Zn_3P_2S_4O_4 + H_2O$ requires S, 27·41 per cent.).

Thallium Dithiophosphate, $Tl_3P_2S_4O_4$.

A solution of thallous carbonate was added to a solution of the the sodium salt, when thallous dithiophosphate was obtained as a yellow precipitate. It was washed with water and finally with alcohol and dried in a vacuum desiccator. The salt is comparatively stable and insoluble in water and alcohol. For estimating thallium a weighed quantity was dissolved in concentrated hydrochloric acid and the solution made almost neutral with the addition of ammonium carbonate. From this solution thallium was estimated as thallous iodide in the usual way. (Found: S, 8·29 ; Tl, 81·46. $Tl_3P_2S_4O_4$ requires S, 8·66; Tl, 82·81 per cent.).

Lead Dithiophosphate, $Pb_3P_2S_4O_4 + 4H_2O$.

The lead compound was obtained as a yellow precipitate by the double decomposition of a solution of sodium dithiophosphate with lead nitrate solution. It was washed with water and finally with alcohol and dried under an electric fan. The lead was estimated by dissolving a weighed quantity of the salt in moderately concentrated hydrochloric acid, and precipitating as sulphide. The sulphide was then converted into the sulphate and estimated as such in the usual way. The sulphur content of the salt was determined in the usual way as barium sulphate after the removal of the lead. (Found: Pb, 35·07 ; S, 13·77. $Pb_3P_2S_2O_3,4H_2O$ requires Pb, 65·58 ; S, 13·52 per cent.).

Unstable Dithiophosphates.

The following dithiophosphates could be obtained as solid precipitates but decomposed either during washing or during drying even in a vacuum desiccator over concentrated sulphuric acid in an ice-chest. All of them were, of course, dithiophosphates and contained both sulphur and phosphorus. The manganous and mercuric salts were also noticed by Kubierschky (*loc. cit.*).

Manganous Dithiophosphate.—The manganous salt was precipitated on the addition of a large excess of manganous sulphate solution to a solution of the sodium salt in the cold. With the addition of small

quantities of manganous sulphate solution at first a green solution, as reported by Kubierschky, was obtained which changed to a white precipitate. The white precipitate was washed with ice water and with cold alcohol. It did not decompose during washing but it was impossible to dry it either under the electric fan or in a vacuum desiccator without decomposition.

Mercuric Dithiophosphate.—The mercuric salt was obtained as a yellow precipitate on the addition of a solution of mercuric chloride to a solution of the sodium salt. It was more unstable than the manganous salt and began to decompose during washing.

Thorium Dithiophosphate.—This compound was obtained as a white precipitate by the double decomposition of a solution of thorium nitrate and a solution of sodium dithiophosphate. The precipitate, however, decomposed during washing with ice water.

Lanthanum Dithiophosphate.—This was obtained as a white precipitate by the double decomposition of a solution of lanthanum nitrate and a solution of sodium dithiophosphate. It too decomposed during washing with ice-water.

We would now conclude by briefly referring to other dithiophosphates, which were obtained as precipitates by double decomposition with the sodium salt but decomposed after a few seconds even when precipitated at 0°. With a solution of sodium dithiophosphate coloured precipitates, which were also noticed by Kubierschky, were obtained with bismuth (yellow), mercury (*ous*) (yellow), copper (green), silver (yellow), cobalt (green), nickel (dirty blue) and cadmium (white) salts. These too were extremely unstable and decomposed within a few seconds of their precipitation. A ferrous compound, not noticed by Kubierschky, was obtained as a yellow precipitate by the addition of a solution of Mohr's salt to a solution of sodium dithiophosphate. The compound was found to be extremely unstable and the final product was the sulphide. Attempts were also made to get the dithiophosphates of aluminium, zirconium and molybdenum by the double decomposition of sodium dithiophosphate and the soluble salts of these metals but the results were negative, only sulphuretted hydrogen being evolved.

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Electrical Conductivity of Salts of Alkaloids in Pure and in Mixed Solvents.

By Jitendra Nath Rakshit.

To study the influence of introduction of alcohol in aqueous solutions of substances on their electrical conductivity, solutes chosen by previous investigators had solubilities in water considerably different from those in alcohol. Solubilities of salts of alkaloids in water and in alcohol being not so much different, it was thought worth while to ascertain how their conductivities would be influenced by the presence of alcohol in their aqueous solutions. The mixtures of solvents used in the present investigation were in molecular proportions, which enabled direct comparison of the molecular-conductivity figures of one solute with those of another. Some of the relevant investigations on the subject may be briefly mentioned in this connection. The conductivity of aqueous solutions of electrolytes is lowered by the addition of alcohol to varying extents (Schall, *Z. physikal. Chem.*, 1894, **14**, 701). The lowering of molecular conductivity of sodium chloride and potassium chloride by the presence of alcohol in their aqueous solution, for 1 per cent. of alcohol, is not so great for the later additions of alcohol as it is for the first additions (Hantzsch, *Z. anorg. Chem.*, 1900, **25**, 332). The conductivity of a salt may be caused to decrease with the rise of temperature by the addition of 1 to 20 per cent. of any aliphatic alcohol (Bartoli, *Gazzetta*, 1894, *ii*, **24**, 156 ; *Abstracts*, 1895, **68**, *ii*, 6).

Conductivities of aqueous-alcoholic solutions of some salts were determined when approximately limiting values were obtained for infinite dilutions in some cases only. Several instances have been found where limiting value for infinite dilution was not obtained (Vollmer, *Ann. Phys. Chem.*, 1894, *ii*, **52**, 3), and instances have also been found where maximum results were obtained (Jones and coworkers, *J. Amer. Chem. Soc.*, 1904, **32**, 521; 1906, **36**, 325). It has been noted by Tymstra (*Abstracts*, 1903, **84**, *ii*, 623) that maximum molecular conductivity is dependent not only on the dilution of the solution but also on the composition of the solvent. Influence of the composition of the solvent, when mixtures of water and alcohol are used, on the molecular conductivities of acids has also been

worked out by Goldschmidt, Schjerve and Feigl (*Z. physikal. Chem.*, 1914, **89**, 129). Arrhenius has investigated many electrolytic aqueous solutions with regard to the influence on their conductivity by the addition of various non-electrolytes in varying quantities (*Z. physikal. Chem.*, 1892, **9**, 487). The decrease of conductivity brought about by the addition of 1 per cent. by volume of the non-electrolyte depends on the nature of both of the electrolyte and of the non-electrolyte.

Cohen's researches are quite interesting in this connection. He noted that dissociation of a substance in aqueous solution could be measured either by the determination of electrical conductivity or by the measurement of the velocity of inversion of cane sugar. But the replacement of some water by alcohol has no effect on the degree of dissociation of the dissolved material as could be determined from the electrical conductivity (Cohen, *Z. physikal. Chem.*, 1898, **25**, 1; 1899, **28**, 145), whereas the velocity of inversion of cane sugar by hydrochloric acid in aqueous solution is diminished by the addition of alcohol.

All the above investigators have tried to generalise using their results in all sorts of ways which are often more or less divergent amongst themselves. This difficulty in arriving at a general conclusion has also been felt in studying the results obtained by the determination of molecular conductivity of hydrochlorides of alkaloids in solution in water, in alcohol and in mixtures of water and alcohol. Conclusion, however, can be drawn under the circumstances that a molecule present in a solution is interdependent to all others present in the field, but it remains to be established to what extent such interdependency is related to or comparable to chemical reaction.

The measurement of molecular conductivity was carried out by the usual method with an induction coil and telephone keeping the cell in a water-bath fitted with an electric stirrer. The temperature of 35° was considered to be suitable for the purpose of such determinations at this tropical place, and this was kept constant throughout the experiment within $\pm 0{\cdot}1°$. Ordinary conductivity water was used in these experiments and the alcohol was purified by refluxing with freshly burnt quick-lime for 3 days, and after distillation had a specific conductivity $6{\cdot}148 \times 10^{-6}$ mhos which agreed well with what was obtained by White (*J. Chem. Soc.*, 1928, **133**, 1413).

Very pure alkaloids were used in the preparation of salts used in these experiments. These pure free bases gave the following molecular conductivities in aqueous solutions prepared by occasionally

shaking finely powered substances with conductivity water for 7 days. Quantities of morphine, codeine and narcotine present in their respective aqueous solutions were determined by evaporation of known volume of each one and the strength of cotarnine in its aqueous solution was ascertained by titration with $N/10$-sulphuric acid.

Molecular conductivities of free bases.

		v	35°
Morphine,	$C_{17}H_{19}O_3N$	556·6	55 4
Codeine,	$C_{18}H_{21}O_3N$	36·8	3·8
Narcotine,	$C_{22}H_{23}O_7N$	2065·0	198 0
Cotarnine,	$C_{12}H_{15}O_4N$	4·16	11·1

Hydrochlorides of morphine, codeine and cotarnine were prepared by neutralising dilute solutions of the acid with dry finely powdered base and recrystallising three times from conductivity water, and finally dried in steam-oven. Narcotine hydrochloride could be conveniently prepared by passing dry hydrochloric acid gas through benzene or alcoholic solution of pure narcotine. Narcotine hydrochloride separates forthwith from benezene solution of the base on passing the acid gas as a white crystalline deposit ; and from the alcoholic solution it separates as fine crystalline mass on evaporation of alcohol on steam-bath. The salt thus prepared, is dried in a steam-oven, powdered and kept in a vacuum desiccator over quicklime over 4 days.

Solvents used in the following determinations of molecular conductivity at 35° were pure water, pure alcohol, or mixtures of water and alcohol in exactly calculated molecular proportions as given below, and dilution of the solutions during a series of measurements was effected by pipettes.

Morphine hydrochloride, $C_{17}H_{19}O_3N,HCl$.

Dilution in litres per gram molecule, (v).	% EtOH mols. ...	0	5	10	30	50	80	90	94	99	100
	% H_2O mols. ...	100	95	90	70	50	20	10	5	1	0
16		94·31	71·36	50·36	30·36	21·17	13·21	—	—	—	—
32		102·11	77·22	56·12	33·41	24·41	17·13	14·21	12·16	12·36	—
64		107·21	82·81	61·41	37·21	30·46	21·22	17·36	16·21	16·21	12·41
128		110·41	84·26	65·26	40·41	34·21	27·13	22·43	21·18	21·81	17·31
256		110·21	90·12	67·36	42·21	34·36	28·41	25·36	27·21	26·41	22·11
512		110·21	90·41	67·17	42·48	33·21	31·30	30·28	31·61	31·21	24·31

Codeine hydrochloride, $C_{18}H_{21}O_3N,HCl$.

16	117·12	87·42	64·21	36·36	26·12	14·12	11·22	11·11	9·31	9·12
32	125·41	95·21	70·23	41·21	30·41	16·14	15·11	14·12	12·41	12·41
64	132·11	99·61	75·41	45·41	36·37	21·41	18·12	18·18	16·21	14·11
128	138·31	104·00	79·42	49·36	40·47	26·26	22·00	22·11	21·41	18·21
256	150·12	106·37	82·37	51·41	43·36	28·20	26·01	24·12	23·21	22·30
512	151·41	109·41	84·41	50·41	43·41	—	—	—	—	—
1024	167·11	113·21	—	—	—	—	—	—	—	—

Narcotine hydrochloride, $C_{22}H_{23}O_7N,HCl$.

Dilution in litres per gram molecule (*v*).	% EtOH mols. ...	0	5	10	30	50	80	90	95	99	100
	% H_2O mols. ...	100	95	90	70	50	20	10	5	1	0
8		193·21	156·21	114·21	71·21	44·23	26·38	20·41	19·32	17·21	14·36
16		216·31	172·30	125·40	81·41	51·34	35·46	24·31	23·41	22·46	16·81
32		225·40	178·71	136·30	87·31	60·68	42·53	29·88	29·24	27·37	20·73
64		246·20	191·83	137·20	92·46	63·71	48·61	35·34	33·21	34·48	25·72
128		254·21	200·74	139·41	94·36	67·31	55·72	42·40	41·26	44·35	28·21
256		256·24	200·81	140·24	94·21	67·40	59·81	54·62	44·34	49·46	35·34
512		258·37	204·01	140·60	94·01	70·81	61·41	52·62	44·28	50·21	—
1024		258·21	209·31	140·40	94·19	—	—	—	—	—	—

Cotarnine hydrochloride, $C_{12}H_{15}O_4N,HCl$.

8		100·41	77·31	58·41	38·12	31·12	25·16	24·11	24·24	23·34	23·14
16		114·17	84·61	63·12	42·41	35·41	30·29	26·12	26·21	25·10	25·16
32		118·48	90·34	66·70	45·62	39·34	34·34	38·11	31·13	31·62	29·21
64		123·41	96·46	69·81	47·21	41·21	38·21	35·41	35·41	36·42	34·32
128		127·61	98·31	73·34	50·34	43·31	39·81	38·32	37·61	39·21	37·45
256		132·10	104·36	74·61	52·17	43·22	44·61	42·41	42·21	42·12	42·36
512		134·07	105·71	74·43	52·12	44·31	44·21	44·36	44·08	44·01	44·42
1024		148·40	113·11	82·32	—	—	—	—	—	—	—

Resistances becoming very great, determinations at higher dilutions of solutions containing large quantities of alcohol were not very accurate. It is seen from these results that these salts of alkaloids are conductors of electricity in solutions in water, in alcohol and in mixtures of water and alcohol. Molecular conductivity decreases as the water in the solution is replaced by alcohol keeping the volume unchanged. Such decreasing influence of alcohol is somewhat similar when solutes are similar in molecular structure but not so when they are different.

If molecular conductivity of codeine hydrochloride in $N/16$-solution in solvents of varying composition from pure water to pure alcohol be divided by that obtained under identical condition of hydrochloride of any other alkaloid, it would be found that the quotients thus obtained are neither constant nor vary uniformly with the variation of the solute. Such variation of results could also be obtained if molecular conductivities of codeine hydrochloride in solutions other than $N/16$ are similarly divided.

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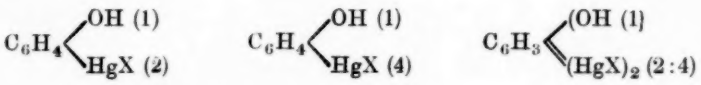
Halogenomercuriphenols.

By John Fernand Caius and Jal Hirji Wadia.

Halogenomercuriphenols are derivatives of benzene characterized by the presence of a nuclear hydroxyl, and by the mercury being linked to a nuclear carbon atom through one valency and to an halogen atom through the other. They are represented by the following types: –



X = halogen.

Desesquelle (*Bull. Soc. Chim.*, 1894, **11**, 263) prepared *p*-chloromercuriphenol by the interaction of potassium phenolate and mercuric chloride. Dimroth (*Ber.*, 1898, **31**, 2155; 1899, **32**, 761) obtained the three chloromercuriphenols by the action of a saturated solution of sodium chloride on the hot filtrate from the interaction of mercuric oxide, glacial acetic acid, and phenol, in hot aqueous solution. Whitmore and Middleton (*J. Amer. Chem. Soc.*, 1921, **43**, 622) prepared the two monochloromercuriphenols by adding a hot solution of sodium chloride to a boiling aqueous solution of the products obtained by heating phenol and mercuric acetate on the steam-bath. Whitmore and Hanson ("Organic Syntheses," 1925, IV, p. 13) obtained *o*-chloromercuriphenol by a method which does not essentially differ from that adopted by Whitmore and Middleton (*loc. cit.*).

By modifying the methods used by those authors we have succeeded in elaborating a general mode of preparation which applies not only to the chloromercuri-compounds, but also to the bromo-, iodo-, and fluoro-mercuri-derivatives. The more salient points are that the mono-derivatives are precipitated in the cold, and that the di-derivatives are obtained from pure crystallised diacetoxymercuriphenol.

The reactions involved are (1) in the case of the monohalogenomercuriphenols,

$$C_6H_5\cdot OH + Hg(OAc)_2 = Ac\cdot OH + OH\cdot C_6H_4\cdot Hg\cdot OAc$$
$$OH\cdot C_6H_4\cdot Hg\cdot O\cdot Ac + NaX = AcO\cdot Na + OH\cdot C_6H_4\cdot HgX$$

and (2) in the case of the dihalogenomercuriphenols,

$$C_6H_5\cdot OH + 2Hg(OAc)_2 = 2Ac\cdot OH + OH\cdot C_6H_3:(Hg\cdot OAc)_2$$
$$OH\cdot C_6H_3:(Hg\cdot OAc)_2 + 2NaX = 2AcO\cdot Na + OH\cdot C_6H_3:(HgX)_2$$

Experimental.

Preparation of Mercuric Acetate.—One kg. of mercuric chloride is added gradually to 580 c.c. of a saturated solution of sodium chloride kept at 95-96°. As soon as the whole has gone into solution, 160 c.c. of a 50 per cent. solution of sodium hydroxide are slowly poured into it with constant stirring. The precipitate is allowed to settle and then the supernatant liquid is siphoned off. The precipitate is washed six or seven times with large amounts of distilled water and freed from sodium hydroxide and sodium chloride. The moist mercuric oxide is dissolved by gradual addition of glacial acetic acid, and the solution kept in the cold chamber at 4–5° The crystals of mercuric acetate are removed and dried as long as the mother-liquor keeps colourless. Yield almost theoretical.

In this method of preparation advantage is taken (1) of the great solubility of mercuric chloride in a saturated aqueous solution of sodium chloride, and (2) of the readiness with which moist mercuric oxide dissolves in acetic acid.

Preparation of the Acetoxymercuriphenols.—100 Gm. of solid phenol are added to 200 gm. of mercuric acetate in 1200 c.c. of water and a few drops of glacial acetic acid. On stirring the substances dissolve and a colourless solution is obtained. Within an hour the insoluble diacetoxymercuriphenol is formed and can be separated by filtration.

(1) The *filtrate* (A) contains a mixture of the soluble *o*- and *p*-acetoxymercuriphenols and is used directly in the preparation of the monohalogenomercuri-compounds.

(2) The *precipitate* on the filter is washed with distilled water (B) at room temperature until (1) the washings give no precipitate or turbidity on addition of an aqueous saturated solution of sodium

chloride—absence of the monoacetoxymercuriphenols, and (2) the precipitate gives no pink colouration with sodium nitrite moistened with a few drops of water—absence of *o*-acetoxymercuriphenol.

Diacetoxymercuriphenol crystallises from 30 per cent. acetic acid in shining plates. Powder gritty white, m.p. 216°. Yield, 102 gm.

Praparation of the Dihalogenomercuriphenols.—Diacetoxymercuriphenol (61 g.) is dissolved in a solution (75 c.c. of a 6·5 per cent.) of sodium hydroxide, filtered through hard ammoniated filter paper. It is shaken with an excess of a saturated solution of the sodium halide, and then treated with acetic acid gradually until the liquid is distinctly acid to litmus. It is filtered, washed free of sodium halide, sodium acetate, or acetic acid, and dried over sulphuric acid in *vacuo*.

Difluoromercuriphenol.—White, soft powder melting at 197·5-198°. Yield, 2·5 gm.. (Found: Hg, 76·16. $C_6H_4OHg_2F_2$ requires Hg, 76·82 per cent.).

Dichloromercuriphenol.—White, slightly gritty powder, unaffected by light or moisture, decomposing at 278°. Yield, 35 gm. (Found: Hg, 70·92. Calc. Hg, 71·12 per cent.).

Dibromomercuriphenol.—White, rough powder, unaffected by light or moisture, turning greyish at 230°. Yield, 5 gm. (Found: Hg, 60·94. $C_6H_4OHg_2Br_2$ requires Hg, 61·44 per cent.).

Di-iodomercuriphenol.—Yellowish, slightly rough powder, affected by light and moisture with slow formation of mercuric iodide, decomposing at 142°. Yield, 12 gm. (Found: Hg, 53·19. $C_6H_4OHg_2I_2$ requires Hg, 53·70 per cent.).

Preparation of the Monohalogenomercuriphenols.—The filtrate (A) and the washings (B) from the preparation of the acetoxymercuriphenols are treated in the cold with an aqueous solution of the sodium halide—saturated in the case of the chloride and the fluoride, 1 : 10 for the bromide, 1 : 100 for the iodide—as long as a precipitate forms. This precipitate is a mixture of *ortho*- and *para*-halogenomercuriphenols together with a small amount of dihalogenomercuriphenol.

1. Boiling water removes the *ortho*-compound which crystallises on cooling. The mother-liquor is then concentrated, and crystals are collected as long as they separate pure.

o-*Fluoromercuriphenol.*—Very small, shining needles ; light drab gritty powder melting at 192·5°. Yield, 2·5 gm. (Found: Hg, 63·71. C_6H_5OHgF requires Hg, 64·16 per cent.).

o-*Chloromercuriphenol.*—Long thick needles ; white rough powder melting at 146-146·5°. Yield, 61·2 gm. (Found: Hg, 60·72. Calc. Hg, 60·95 per cent.).

o-*Bromomercuriphenol.*—Short needles in rosettes ; white soft powder melting at 121·5—122°. Yield, 8·9 gm. (Found: Hg, 53·25. C_6H_5OHgBr requires Hg, 53·72 per cent.).

o-*Iodomercuriphenol.*—Long shining silky needles ; white, soft powder melting at 106·5°. Yield, 3 gm. (Found: Hg, 47·09. C_6H_5OHgI requires Hg, 47·93 per cent.).

2. The *para*-compound is extracted with boiling absolute alcohol from which it crystallises on standing.

p-*Fluoromercuriphenol* does not crystallise ; white, soft powder melting at 204°. Yield, 3 gm. (Found: Hg, 63·36. C_6H_5OHgF requires Hg, 64·16 per cent.).

p-*Chloromercuriphenol.*—Large plates ; white rough powder melting at 216°. Yield, 22 gm. (Found: Hg, 60·32. Calc. Hg, 60·95 per cent.).

p-*Bromomercuriphenol.*—Large glistening flakes ; white, gritty powder changing colour at 185°, without melting. Yield, 8·6 gm. (Found: Hg, 53·35. C_6H_5OHgBr requires Hg, 53·72 per cent.).

p-*Iodomercuriphenol.*—Large shining flakes ; white, slightly rough powder turning golden yellow at 180° without melting. Yield, 56·5 gm. (Found: Hg, 47·58. C_6H_5OHgI requires Hg, 47·93 per cent.).

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Oxidation of Carbohydrates, Fats and Nitrogenous Substances by Hydrogen Peroxide and Ferric Salts.

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In a series of publications from this laboratory, the slow and induced oxidation of organic and inorganic substances has been investigated (*Z. anorg. Chem.*, 1922, **122**, 146 ; 1925, **144**, 289 ; *J. Phys. Chem.*, 1924, **28**, 943 ; 1925, **29**, 376, 799 ; 1926, **30**, 939 ; 1928, **32**, 1263, 1663) and the mechanism of the oxidation in the animal body has been imitated. It is well known that the edible substances like carbohydrates, fats and proteins are very readily oxidised in the body, whereas they are oxidised with difficulty in the laboratory. But in the papers referred to, it has been shown that the edible substances can be oxidised in the laboratory also at the ordinary temperature by passing air, if inductors like ferrous hydroxide, cerous hydroxide, sodium sulphite, etc., are present. It is interesting to note that these edible substances can be oxidised by passing air through them if they are exposed to sunlight even without any catalyst. In each of these cases, complete oxidation to carbon dioxide takes place. Even complex substance like butter, lecithin, milk, egg-white, egg-yellow, cholesterol, etc., are oxidised almost quantitatively into carbon dioxide and water.

We know that a deviation from this rule is found in animal bodies during certain diseases and also during fasting. In diabetic patients, glucose is practically not oxidised and acetone bodies are found in the organism. In normal health, the heat and energy of the body is derived from the simultaneous and slow combustion of carbohydrates, fats and nitrogenous substances. But in diabetes, the carbohydrates are not oxidised. Hence, in order to supply the necessary heat and energy to the body, the oxidation of fats and nitrogenous substances has to become more rapid than in normal health. It appears, therefore, that when the oxidation of fats and nitrogenous substances is more rapid than in normal health, acetone bodies are likely to be formed. The acetone bodies are also formed during long fasting. In starvation, the necessary amount of heat and energy is obtained from the body itself and the glycogen store in the body is first oxidised. When the glycogen is exhausted, in order to bring in the same amount of energy, a more rapid oxidation of the body tissues and body fats takes place with the result that acetone bodies

are formed. Dakin (*J. Biol. Chem.*, 1908, **4**, 77) had shown that ammonium butyrate, on being oxidised with hydrogen peroxide, produced acetone, acetoacetic acid, acetaldehyde, etc. As hydrogen peroxide is believed to be a more rapid oxidising agent than air, it was thought desirable to investigate the oxidation of edible substances with hydrogen peroxide and ferric salt as an accelerator, in order to find out the nature of the change occurring if the oxidation in animal body becomes more rapid than in normal health. In the present paper, the oxidation of edible substances either occurring singly or in mixtures, by hydrogen peroxide and ferric salt, has been investigated and our results are likely to throw considerable light on the metabolism in diabetes and in starvation.

In several publications from these laboratories we have proved that the slow oxidation of substances can be retarded by another reducing agent which usually undergoes slow oxidation along with the primary change (*Proc. Akad. Wet., Amsterdam*, 1921, **29**, 1023; *Z. anorg. Chem.*, 1925, **144**, 289; *cf.* Moureau and Dufraisse, *Compt. rend.*, 1924, **179**, 237). Thus we have shown that the oxidation of sodium sulphite by air is markedly retarded by sodium arsenite which undergoes oxidation by air in presence of sodium sulphite. Similarly we have proved that the slow oxidation of carbohydrates by air is retarded by fats and nitrogenous substances and the oxidation of fats and nitrogenous substances is retarded by the presence of glucose. In the present paper, we have also investigated the retardation of the oxidation of one edible substance by hydrogen peroxide in presence of another.

Experimental.

10 C.c. of 1% solution of carbohydrates, fats and nitrogenous substances were mixed with 10 c.c. of hydrogen peroxide (Merck's, 12% by vol.) and 1 c.c. of ferric sulphate solution containing 0·005 gm. of iron. The mixture was kept at 37° (body temperature) in a thermostat for 5 hours. The products were carefully distilled by heating the mixture for forty-five minutes over the direct flame of a Bunsen burner. The distillate and the residue were treated with the following reagents: – (*i*) Fehling's solution; (*ii*) Schiff's reagent, (*iii*) mercuric chloride, (*iv*) ammoniacal silver nitrate, (*v*) bromine water, (*vi*) calcium chloride and (*vii*) iodine with caustic soda. The smell of the products was also noted. The results are tabulated in the Table I.

TABLE I.

Reactions with Various Reagents after Oxidising Different Organic Substances with H_2O_2.

Reagents.	Potassium stearate.		Potassium oleate.		Potassium palmitate.		Glucose.		Starch.		Alanine.		Lactic acid.	
	0·1 gm.		0·1 gm.		0·1 gm.		0·1 gm.		0·1 gm.		0·1 gm.		0·1 gm.	
	Distillate.	Residue.	Distillate.	Residue.	Distillate.	Residue.	Distillate.	Residue.	Distillate.	Residue.	Distillate.	Residue.	Distillate.	Residue.
Fehling's solution.	Reduced	...	Reduced	...	Reduced	...	Reduced	Reduced	...	Reduced	Reduced	...	Reduced	...
Schiff's reagent.	...	...	...	...	...	...	...	...	...	...	Pink	...	Pink	...
Mercuric chloride.	...	Reduced	Reduced	Reduced	...	Reduced	Reduced	Reduced	Reduced	Reduced	Reduced	Reduced	Reduced	Reduced
Am. silver nitrate.	Reduced	...	Reduced	...	Reduced	...	Reduced	Reduced	Reduced	Reduced	Reduced	Reduced	Reduced	Reduced
Bromine water.	Decolorised.	...	Decolorised.	...	Decolorised.	...	Decolorised.	...	...	...	Decolorised.	...	Decolorised.	...
Calcium chloride.	...	White ppt.	...	White ppt.	...	White ppt.	...	...	...	...	...	...	...	...
Alkaline iodine.	Iodoform	...	Iodoform	...	Iodoform	...	...	...	...	...	Iodoform	...	Iodoform	...
Smell	Acrolein	...	Acrolein	...	Acrolein	...	...	...	...	...	Acetaldehyde.	...	Acetaldehyde.	...

In the cases of potassium palmitate, stearate and oleate, the smell of acrolein could be distinctly perceived in the distillate, and in the last case, the smell was very strong. In the case of lactic acid and alanine, a distinct smell of acetaldehyde was found. But in the majority of cases the products could not be definitely identified because they contain numerous ingredients. The volatile aldehydic and ketonic products were estimated in the following way : –

The above mixture of the edible substances, hydrogen peroxide and ferric salt, after keeping at 37° for 5 hours, was taken out and the volume was made up to 50 c.c. in every case. They were then distilled slowly for 45 minutes in the usual way and the distillate absorbed in water. 10 C.c. of $N/10$-caustic soda and 10 c.c. of $N/10$-iodine solution were then added to the distillate and kept aside for ten minutes. A portion of the iodine was taken up by the aldehydic products and iodoform was produced in appreciable quantities in the cases of fats, and some nitrogenous substances. The solution was acidified with 10 c.c. of $N/10$-sulphuric acid and the liberated iodine was titrated against $N/10$-sodium thiosulphate, thus giving the amount of iodine taken up by the volatile products. The results are given in Tables II—V.

TABLE II.

Carbohydrate taken=0·1 gm. Hydrogen peroxide=10 c.c. Amount of iron in ferric sulphate=0·005 gm. Time of oxidation=5 hrs. Temperature=15°. Total volume =50 c.c.

Carbohydrate :	Glucose.	Fructose.	Lactose.	Arabinose.	Galactose.	Maltose.
Amount of $N/10$-iodine absorbed :	2·6 c.c.	3·2 c.c.	3·8 c.c.	3·5 c.c.	4·2 c.c.	6·0 c.c.

Carbohydrate :	Sucrose.	Starch.	Dextrin.	Inulin.	Glycogen.
Amount of $N/10$-iodine absorbed :	1·7 c.c.	2·6 c.c.	3·3 c.c.	3·3 c.c.	4·2 c.c.

TABLE III.

Nitrogenous substance taken=0·1 gm. (0·5 gm in the case of urea). Hydrogen peroxide=10 c.c. Amount of iron in ferric sulphate=0·005 gm. Time of oxidation=5 hrs. Temperature=37°. Total volume=50 c.c.

Nitrogenous substance :	Alanine.	Glycine.	Egg-white.	Egg-yellow.	Urea.
Amount of $N/10$-iodine absorbed in c.c. :	3·70	3·40	3·80	3·30	nil

TABLE IV.

Amount of fats taken = 0·1 gm. (0·462 gm. in the case of butter).
Hydrogen peroxide = 10 c.c. (20 c.c. in the case of butter).
Amount of iron in ferric sulphate = 0·005 gm.
Time of oxidation = 5 hrs. (24 hrs. in the case of butter).
Temperature = 37°. Total volume = 50 c.c.

Fats :	K-oleate.	K-stearate.	K-palmitate.	Butter.
Amount of $N/10$-iodine absorbed in c.c. :	4·9	2·4	4·6	5·6

TABLE V.

Cholesterol + *Hydrogen Peroxide* + $Fe_2(SO_4)_3$.

Volume = 50 c.c.

Amount of cholesterol.	Amount of H_2O_2.	Amount of iron	Temp.	Time.	Amount of $N/10$-iodine absorbed.
0·5 g.	20 c.c.	0·009 g.	37°.	24 hrs.	2·6 c.c.

The mutual retardation in the oxidation of the food materials with hydrogen peroxide and ferric salt was measured in the following way: 10 c.c. each of carbohydrates and nitrogenous substances were mixed and 20 c.c. of hydrogen peroxide were added. The temperature was kept at 37° but the time of the reaction was extended to 25 hours. After the reaction, the volume was made up to 100 c.c. and the distillation carried on for about an hour and a quarter. The distillate was absorbed in water and 20 c.c. of $N/10$-NaOH and 20 c.c. of $N/10$-iodine were added and the residual iodine estimated in the usual way. Similar treatment was made in the mixtures of carbohydrates and fats, and fats and nitrogenous substances. In the mixture of all the three varieties, the amount of hydrogen peroxide was increased to 20 c.c., and the time was extended to 48 hours. The results are tabulated in Tables VI–XI.

TABLE VI.

Carbohydrates + *Nitrogenous Substances* + H_2O_2 + $Fe_2(SO_4)_3$.

Hydrogen peroxide = 20 c.c. Carbohydrate = 0·1 gm. Nitrogenous matter = 0·1 gm.

Iron = 0·005 gm. Temperature = 37°. Time = 24 hours. Total volume = 100 c.c. Egg-white or yellow = 0·5 gm.

Carbohydrates.	Alanine (3·7).	Glycine (3·4).	Urea (*x*).	Egg-white (3·8).	Egg-yellow. (3·3).
Glucose (2·6)	5·3 c.c.	3·6 c.c.	2·5 c.c.	3·1 c.c.	1·9 c.c.
Fructose (3·2)	3·7	2·1	...	2·3	3·2
Lactose (3·8)	4·0	3·6	...	1·6	6·7
Arabinose (3·5)	1·9	3·7	...	4·4	4·8
Galactose (4·2)	4·7	4·4	...	4·8	5·1
Maltose (6·0)	5·2	4·2	...	1·9	6·2
Sucrose (1·7)	3·2	2·9	...	2·1	6·2
Starch (2·6)	1·8	4·8	...	3·3	3·7
Inulin (3·3)	2·7	3·1	...	2·7	3·5
Dextrin (3·3)	4·8	2·4	...	2·5	5·3
Glycogen (4·2)	3·9	4·3	...	2·6	5·9

N. B.—The figures in the brackets in the above and all subsequent tables show the amount of *N*/10-iodine absorbed by the single substance after oxidation. The other figures indicate the amount of *N*/10-iodine absorbed by the mixtures after oxidation.

TABLE VII.

Carbohydrates + Fats + Hydrogen Peroxide + $Fe_2(SO_4)_3$.

Hydrogen peroxide = 20 c.c. Carbohydrate = 0·1 gm. Fat = 0·1 gm. (butter = 0·462 gm.) Iron = 0·005 gm. Temperature = 37°. Time = 25 hours (72 hrs. in the case of the mixture with butter). Total volume = 100 c.c.

	K-oleate (4·9)	*K*-stearate (2·4)	*K*-palmitate (4·6)	Butter (5·6)
Glucose (2·6)	6·2 c.c.	2·6 c.c.	4·7 c.c.	6·3 c.c.
Fructose (3·2)	1·1	1·9	4·6	3·9
Lactose (3·8)	4·6	4·6	3·8	5·9
Arabinose (3·5)	5·5	3·3	2·1	6·7
Galactose (4·20)	5·7	4·3	5·3	5·6
Maltose (6·0)	5·7	2·0	4·5	6·0
Sucrose (1·7)	2·2	1·3	1·7	5·1
Starch (2·6)	2·5	1·1	2·2	4·9
Inulin (3·3)	6·3	5·6	6·0	6·0
Dextrin (3·3)	3·2	3·6	3·6	3·2
Glycogen (4·2)	6·7	6·4	6·0	3·7

TABLE VIII.

Fats + Nitrogenous Substances + Hydrogen Peroxide + $Fe_2(SO_4)_3$.

Hydrogen peroxide = 20 c.c. Fats = 0·1 gm. (butter = 0·462 gm). Nitrogenous substances = 0·1 gm. (egg-white or -yellow = 0·5 gm). Iron = 0·005 gm. Temperature = 37°. Time = 25 hours (72 hrs. in the case of the mixture with butter). Total volume = 100 c.c.

	Alanine. (3·7)	Glycine. (3·4)	Urea. (*x*)	White-egg. (3·8)	Egg-yellow. (3·3).
Potassium oleate (4·9)	4·6 c.c.	2·3 c.c.	2·9 c.c.	3·3 c.c.	6·6 c.c.
Potassium stearate (2·4)	2·1	3·5	2·2	3·8	6·9
Potassium palmitate (4·6)	4·1	3·1	1·2	6·4	6·7
Butter (5·6)	4·4	6·7	...	4·4	6·5

TABLE IX.

Cholesterol + Fats + Hydrogen Peroxide + $Fe_2(SO_4)_3$.

Hydrogen peroxide = 30 c.c. Fats = 0·1 gm. Cholesterol = 0·5 gm. Iron = 0·005 gm. Temperature = 37°. Time = 60 hours. Total volume = 100 c.c.

	Potassium stearate. (2·4)	Potassium palmitate. (4·6)	Potassium oleate. (4·9)
Cholesterol (2·6)	4·0 c.c.	5·6 c.c.	4·7 c.c.

TABLE X.

Carbohydrates + Fats + Nitrogenous Substances + Hydrogen Peroxide + $Fe_2(SO_4)_3$.

Carbohydrates, oleate, stearate and palmitate = 0·1 gm. each. Butter = 0·462 gm. Egg-white or -yellow = 0·5 gm. each. Hydrogen peroxide = 30 c.c. Iron = 0·005 gm. Temperature = 37°. Time = 53 hours. Total volume = 100 c.c.

Mixtures.			Amount of *N*/10-iodine absorbed.
Glycogen (4·2)	+ Alanine (3·7)	+ Oleate (4·8)	6·0 c.c
,,	,,	+ Stearate (2·5)	4·8
,,	,,	+ Palmitate (4·4)	6·1
Butter (5·6)	+ Egg-white (3·8)	+ Glucose (2·6)	5·3
,,	,,	+ Sucrose (1·7)	3·1
,,	,,	+ Starch (2·6)	5·2
,,	,,	+ Inulin (3·3)	3·6
,,	,,	+ Dextrin (3·3)	5·6
,,	,,	+ Glycogen (4·2)	3·8

TABLE X—*contd.*

Mixtures.	Amount of *N*/10-iodine absorbed.
Butter (5·6) + Egg-yellow (3·3) + Glucose (2·6)	8·3 c.c.
,, ,, + Sucrose (1·7)	7·3
,, ,, + Starch (2·6)	6·6
,, ,, + Inulin (3·3)	9·6
,, ,, + Dextrin (3·3)	8·6
,, ,, + Glycogen (4·2)	6·8

TABLE XI.

Carbohydrates + Fats + Hydrogen Peroxide + $Fe_2(SO_4)_3$.

Hydrogen peroxide = 75 c.c. Carbohydrate = 0·5 gm. Oleate = 0·2 gm. Butter = 0·925 gm. Iron = 0·005 gm. Temperature = 37°. Time = 50 hours. Total volume = 150 c.c.

Mixtures.	Amount of *N*/10-iodine absorbed.
Glucose (12) + Oleate (10·1)	8·2 c.c.
Starch (12·2) ,,	5·3
Sucrose (9) ,,	5·1
Dextrin (15) ,,	7·4
Glycogen (19·8) ,,	6·9
Inulin (15·2) ,,	8·4
Glucose (12) + Butter (11·5)	9·9
Starch (12·2) ,,	5·6
Sucrose (9) ,,	5·5
Dextrin (15) ,,	7·8
Glycogen (19·8) ,,	8·3
Inulin (15·2) ,,	9·8

A glance at the above table shows that in each case a certain amount of iodine has been taken up by the volatile product showing that substances of aldehydic or ketonic nature have been produced during the reaction. The amount of the substances of aldehydic or ketonic nature formed is greatest in the case of fats, specially butter and least in the case of carbohydrates, specially sucrose. It is interesting to note that not only do the fats and nitrogenous substances produce compounds of aldehydic or ketonic nature but even the carbohydrates produce substances of this type. The explanation is not far to seek. The carbohydrates on oxidation gives rise to glyceric aldehyde, pyruvic aldehyde, pyruvic acid and lactic acid. Lactic acid

very easily oxidises to acetaldehyde (*cf.* Ray, *J. Gen. Physiol.*, 1924, **6**, 509, 528).

The higher fatty acids gradually oxidise into the lower fatty acids due to β-oxidation (*Beitr. Chem. Physiol. Path.*, 1908, **22**, 411) and ultimately to butyric acid from which the production of acetone bodies can be explained. The amino-acids on oxidation give the hydroxy-acids, the lower acids and ultimately aldehydic and ketonic products. It has been known from a long time that alanine can produce acetaldehyde on oxidation, and hence if the proteins hydrolyse to the stage of amino-acids, as it usually does in the body, the production of alanine or similar products can explain the formation of acetone bodies from the proteins.

It is interesting to note from the foregoing data that, in mixtures, the amount of iodine absorbed by the volatile products after oxidation with hydrogen peroxide is remarkably reduced showing that the amount of the substances of aldehydic nature is decreased. The retardation is greatest in the case of starch and sucrose. Table XI shows that if the amount of carbohydrates be increased the amount of aldehydic product is still more decreased. Hence the presence of carbohydrates decreases the amount of acetone bodies formed by the oxidation of fats by hydrogen peroxide and ferric salts.

It appears therefore that some methods of treatment in diabetes are faulty. A school of medical men prefer the administration of fats to diabetic patients arguing that as glucose cannot be oxidised in the body, the required energy must be supplied by fat. But our results show that in the absence of glucose, fats cannot be oxidised in the normal manner. On the contrary, they produce poisonous bodies like acetone, diacetic acid, etc. So the more the patient gets fats, the more is the quantity of acetone bodies formed and thus the end of the patient is likely to be hastened. Similar arguments can be brought against those who prefer protein ingestion. In order that the oxidation in the animal body should proceed in the normal manner, glucose must be oxidised. So the treatment of diabetic patients should depend upon the fundamental principle that the glucose must be more largely oxidised.

It is well known that by the injection of insulin, acetone bodies disappear from the body. This is due to the fact that by the presence of insulin, the glucose, which was passing unoxidised from the diabetic system, is oxidised and the oxidation of the glucose leads to the more complete though more slow oxidation of fats.

Summary.

(1) Sugars, starch, glycogen, dextrin, inulin, alanine, egg-white, egg-yellow, butter, oleate, stearate, palmitate, etc., were oxidised with hydrogen peroxide and ferric salt and the volatile aldehydic or ketonic products were estimated by the amount of iodine taken up by them in the formation of iodoform. It has been proved that not only the fats but the carbohydrates and nitrogenous substances have the property of producing acetone bodies.

(2) The oxidation of the mixtures of fats and proteins fats and carbohydrates, carbohydrates and proteins and the mixture of all the three varieties by hydrogen peroxide and ferric salt has been investigated and it has been shown that in mixtures, the amount of acetone bodies formed is markedly decreased. Thus the oxidation of fat is retarded by proteins and carbohydrates, the oxidation of protein is retarded by carbohydrates and fats and the oxidation of carbohydrates is retarded by fats and proteins.

(3) It has also been shown that in the oxidation of the mixtures of carbohydrates and fats with hydrogen peroxide and ferric salt, the amount of acetone bodies is decreased with the increase of the amount of carbohydrates.

(4) These experimental results are likely to throw considerable light on the metabolism in the animal body in normal health, in diabetes and in starvation.

(5) It seems that the disappearance of acetone bodies from the diabetic organism due to the injection of insulin is caused by the increased oxidation of the negative catalyst glucose.

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Use of Phenolic Acids in the Detection, Separation and Estimation of Metals. Part I. A New Qualitative Method for the Separation of 2A Group (Analytical) Metals.

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The usual qualitative separation of 2A group metals is well known. In the proposed method the principle of separation of mercury from the rest of the metals is kept as usual and the new method is applied in the separation of lead, bismuth, copper and cadmium. The principles are based on the following facts:

(*i*) In dilute nitric acid solution gallic acid completely precipitates bismuth, whereas lead, copper and cadmium are unaffected, thus separating bismuth from the rest.

(*ii*) In neutral or faintly acid (nitric) solution gallic acid and sodium acetate completely precipitate lead and copper. Thus lead and copper are separated from cadmium.

(*iii*) In neutral or dilute nitric acid solution, hydrogen peroxide and ammonia completely precipitate lead (Das-Gupta, Roy and Sil, *J. Indian Chem. Soc.*, 1928, **5**, 657), copper remaining in solution. This separates lead from copper.

When the question of precipitating the 2A group metals as sulphide does not arise, which is rarely the case, then, according to the new method, their separation is carried out by following the principles given below:—

(*a*) In dilute nitric acid solution of the metals, resorcylic acid completely precipitates mercury alone (separation of mercury from the rest).

(*b*) For the separation of bismuth, lead, copper and cadmium the principles mentioned in (*i*), (*ii*) and (*iii*) are followed.

In the existing method of separation, the rapidity of the process is greatly hampered in separating lead (as sulphate) from bismuth, copper and cadmium, whereas following the proposed method, the whole course of separation can be finished in much less time. Also,

this method enables one to separate copper from cadmium. Further, the use of the poisonous chemical, potassium cyanide, is altogether avoided.

The action of three phenolic acids (tannic, gallic and resorcylic) on nitrates, chlorides, acetates and sulphates of the metals of 2A group has been thoroughly studied. It has been found that gallic and resorcylic acids are most suitable for the separation of the above metals. The nature of the precipitates obtained in the cases of mercury, bismuth, lead and copper by resorcylic acid, gallic acid and gallic acid + sodium acetate respectively, is under investigation. Further work on the separation and estimation of the metals of 2A group is in progress.

Experimental.

Solutions of the nitrates of mercury, bismuth, lead, copper and cadmium are prepared, of which the nitrate solutions of mercury and bismuth are acidic (due to free nitric acid required in the process of solution). In the solutions the amount of the respective metals present per c. c. is determined by the standard methods. With these solutions a study of the separation of 2A group metals is carried on as follows.

Action of Gallic Acid on Bismuth Nitrate Solution.

(1 c. c. $=0{\cdot}0114$ g. Bi; Free mineral acidity $=N/6$ nearly).

When a fresh 1% solution of gallic acid is added to the bismuth nitrate solution, at first a yellowish white bulky precipitate is formed: this, on warming, becomes crystalline (light yellow) and settles quickly. When a warm solution of bismuth nitrate is employed the precipitate readily becomes crystalline. But when both the reactants are hot, the light yellow crystalline precipitate is formed. The precipitate is insoluble in water, but soluble in dilute mineral acids or in excess of dilute acetic acid. On igniting the precipitate, organic matter is seen to burn and metallic bismuth is formed with the usual yellow oxide incrustration.

It has been found that gallic acid completely precipitates bismuth from the solution, when the concentration of acid (nitric) is $N/18$ or the total concentration of the acid after the addition of the reagent is $N/14$.

To prove this conclusively, the bismuth precipitate is treated with warm $N/10$- and $N/14$- nitric acids, with the result that the filtrate from $N/10$-acid shows the presence of traces of bismuth only whereas the filtrate from $N/14$-acid shows its complete absence. From the above, the conditions for the quantitative precipitation of bismuth from a solution of its nitrate stand as follows: –

(*a*) The solution should not contain more than free mineral (nitric) acidity of $N/18$.

(*b*) For each 0·1 g. bismuth present, the volume of the solution should not be less than 30 c. c.

It has also been observed that a suspension of bismuth hydroxide or bismuth oxynitrate reacts with warm gallic acid solution producing the usual light-yellow crystalline precipitate. In this connection it should be noted that for the precipitation of bismuth, the solution must be absolutely free from chloride, in the presence of which gallic acid produces practically no precipitate.

Action of Gallic Acid on Lead Nitrate Solution.
(1 c.c. = 0·02494 g. Pb).

When 1% gallic acid is added to lead acetate solution, an immediate white bulky precipitate with yellowish tinge is obtained, which on warming becomes crystalline and light yellow in colour and settles very quickly. But when lead nitrate solution is taken instead of the acetate, no precipitate is obtained, but on adding sodium acetate solution to this, a light yellow precipitate is obtained. This non-appearance of precipitate in lead nitrate solution is evidently due to the free nitric acid, liberated in the course of the reaction. It has been found that 1 c.c. of the lead nitrate solution, even when diluted to 100 times, produces no precipitate on the addition of the reagent. This behaviour helps the separation of bismuth from lead.

It has also been observed that gallic acid together with sodium acetate can effect a quantitative precipitation of lead from a warm and neutral solution of its nitrate provided that for each 0·025 g. of lead, the volume of the solution is not less than 15 c.c. In the case of acid (nitric) solution, quantitative precipitation can also be obtained provided that the free acidity is not more than $N/200$; for qualitative analysis free acidity of $N/100$ is quite satisfactory.

Experiments on the Quantitative Precipitation of Lead from its Nitrate Solution (Neutral or Acidic).

Neutral Solution.

Lead nitrate solution = 1 c.c. Sodium acetate (5%) = 2 c.c.

Expt.	Water c.c.	Gallic acid : 1% soln. c.c.	Total vol. c.c.	Dilution.	Liberated acidity calculated from the amount of Pb.	Remarks.
1	10	5	18	1/18	$N/72$	Lead almost absent.
2	15	5	23	1/23	$N/92$	Lead absent
3	15	2	20	1/20	$N/80$	,,
4	20	5	28	1/28	$N/112$	,,
5	25	5	33	1/33	$N/132$	,,
6	10	3	16	1/16	$N/64$	Lead almost absent.
7	16	1	20	1/20	$N/80$	Much lead present.

Acid Solution.

Lead nitrate solution = 1 c.c. Sodium acetate (5%) = 3 c.c.
Gallic acid (1%) = 5 c.c. Total volume = 33 c.c.

Expt.	$N/10$-HNO_3 c.c.	Water. c.c.	Free acidity.	Total acidity in the soln. after the reaction.	Remarks.
I	2·5	21·5	$N/100$	$\left(\frac{N}{10}\times\frac{2\cdot5}{33}+\frac{N}{4}\times\frac{1}{33}\right)=\frac{N}{66}$	Lead almost absent.
II	1·25	22·75	$N/200$	$\left(\frac{N}{10}\times\frac{1\cdot25}{33}+\frac{N}{4}\times\frac{1}{33}\right)=\frac{N}{88}$	Lead absent.
III	0·625	23·375	$N/400$	$\left(\frac{N}{10}\times\frac{0\cdot625}{33}+\frac{N}{4}\times\frac{1}{33}\right)=\frac{N}{106}$	,,

In all the experiments, sodium acetate is added gradually to the warm lead nitrate solution to which an excess of gallic acid has been added.

From Expts. 3 and 7 it is clear that for each 0·025 g. of lead at least 2 c.c. of 1% gallic acid should be used. In the case of acid solution, enough sodium acetate is added to produce a turbidity followed by 2 c.c. more.

The precipitate of lead, like that of bismuth, is insoluble in water and soluble in dilute acids. The solubility in mineral acids

is far greater than in acetic acid. Like the bismuth precipitate metallic lead is formed with yellow oxide incrustration on ignition.

Action of Gallic Acid on Copper Nitrate Solution.
(1 c.c. = 0·0239 g. Cu).

Gallic acid when added to a neutral solution of copper nitrate in the cold produces no change, but, when heated above 55°, the solution becomes turbid (brownish) and on boiling a part of the copper is thrown down as a chocolate-brown precipitate. If, however, the copper solution contains a little free nitric acid ($N/200$ or more) no change is produced even on boiling with gallic acid ; with a concentration of $N/400$-acid, a change in the colour of the solution is produced but no precipitation. With acetic acid, an acidity of $N/1$ or more can prevent the formation of the precipitate of copper. These observations make the separation of copper from bismuth possible. It should be noted, however, that as in the case of lead, copper can be precipitated completely from a solution of its nitrate by gallic acid and sodium acetate. In this case the precipitate is voluminous and is coloured chocolate-brown and takes longer time for settling.

For the complete precipitation of copper by gallic acid and sodium acetate, it is found that, in the copper nitrate solution, having free mineral acidity of $N/14$ after the addition of just excess gallic acid, an excess of sodium acetate can quantitatively precipitate 0·024g. of copper present in a volume of 25 c.c. In this case at least 4 c.c. of 1% gallic acid are required for 0·024 g. of copper. In this connection it should be noted that when both lead and copper are present in a solution, for the complete precipitation of lead with copper, the solution should be so diluted that the resultant acidity (acetic) will not be more than $N/66$.

The precipitate of copper, on ignition, leaves black cupric oxide. It is insoluble in water.

Action of Gallic Acid on Cadmium Nitrate Solution
(1 c.c. = 0·0199 g. Cd).

It has been found that acidic or even neutral cadmium nitrate solution produces no change at all with gallic acid and sodium acetate. This behaviour of cadmium nitrate solution renders its separation from bismuth, lead and copper possible.

The non-appearance of precipitate in the case of cadmium suggests its extreme solubility in acetic acid.

Action of β-Resorcylic Acid on Mercuric Nitrate Solution.
(1 c. c. = 0·02109 g. Hg).

Gallic acid, under the conditions, for the complete precipitation of bismuth, produces with mercuric nitrate solution, an orange precipitate, in the cold, which, on warming, becomes dirty-brown. Thus separation of mercury from lead, copper and cadmium may be possible but not from bismuth. It has, however, been found that using resorcylic acid instead of gallic acid, mercury can be quantitatively precipitated leaving bismuth, lead, copper and cadmium in solution. Thus the separation of mercury from these metals is possible. After separating mercury, the separation of bismuth, lead, etc., can be carried on as stated before.

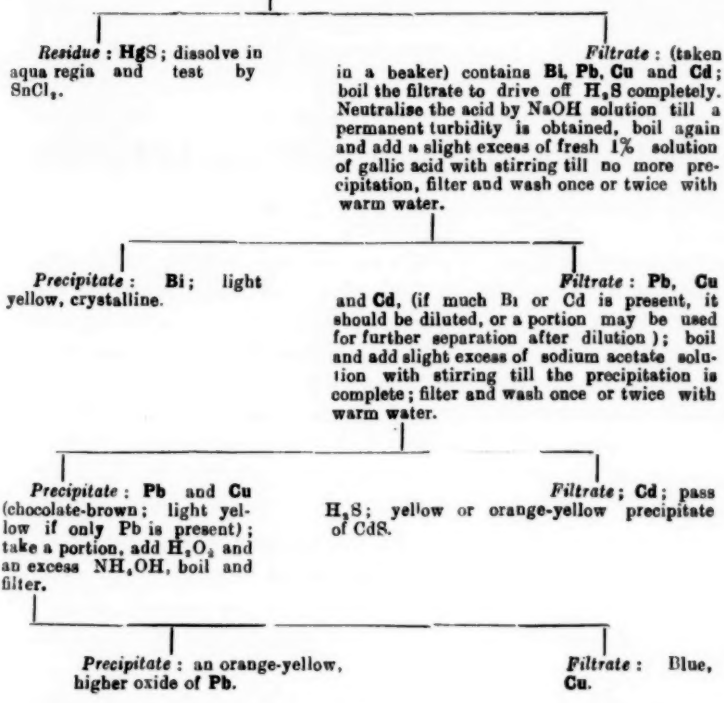
Resorcylic acid in a faintly acid (nitric) solution of mercuric nitrate, produces a flocculent white precipitate ; this, on warming, becomes granular having a faint yellowish tinge, and settles quickly. The precipitate is soluble in dilute mineral and glacial acetic acids, but insoluble in cold or hot water. In precipitating mercury completely from a solution of its nitrate, a solution of β-resorcylic acid saturated in the cold is used in excess (at least 2 c. c. of the solution is required for 0·02 g. of mercury). The solution should not contain more than $N/100$ free acidity (nitric) and for each 0·1g. mercury, the volume should not be less than 40 c. c.

From the above experimental facts, the separation of the metals of 2A analytical group can be easily carried out. The possibility of adsorption of other substances by the precipitates does not materially affect their qualitative separation and detection. However, adjusting the acidity of the wash liquids for the respective precipitates, the adsorption, if any, can be completely avoided.

From the study of the action of the phenolic acids on solutions of lead and copper nitrates, it is found that their separation by any *one* of the acids is not possible. On dissolving the lead-copper precipitate in a minimum quantity of dilute nitric acid and adding hydrogen peroxide and an excess ammonia and then on boiling, or simply boiling the precipitate with hydrogen peroxide and an excess of ammonia, lead can be precipitated and separated from copper as a yellow or an orange-yellow higher oxide of the type Pb_xO_y, zH_2O, where $y > x$.

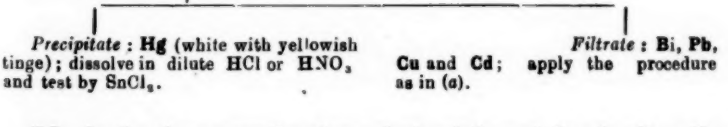
The procedure of separation of the 2A group metals (*a*) when required to be precipitated as sulphides, or (*b*) when all of them are present in nitric acid solution, is shown in a tabular form.

(*a*) The precipitated sulphides of Hg, Bi, Pb, Cu and Cd are digested (in a basin) with dilute nitric acid (6*N*) and then filtered and washed with cold water,


Residue : HgS ; dissolve in aqua regia and test by $SnCl_2$.
Filtrate : (taken in a beaker) contains Bi, Pb, Cu and Cd; boil the filtrate to drive off H_2S completely. Neutralise the acid by NaOH solution till a permanent turbidity is obtained, boil again and add a slight excess of fresh 1% solution of gallic acid with stirring till no more precipitation, filter and wash once or twice with warm water.
Precipitate : Bi; light yellow, crystalline.
Filtrate : Pb, Cu and Cd, (if much Bi or Cd is present, it should be diluted, or a portion may be used for further separation after dilution); boil and add slight excess of sodium acetate solution with stirring till the precipitation is complete; filter and wash once or twice with warm water.
Precipitate : Pb and Cu (chocolate-brown; light yellow if only Pb is present); take a portion, add H_2O_2 and an excess NH_4OH, boil and filter.
Filtrate; Cd; pass H_2S; yellow or orange-yellow precipitate of CdS.
Precipitate : an orange-yellow, higher oxide of Pb.
Filtrate : Blue, Cu.

N.B.—When lead is absent, then the nitrate solution can be neutralised by NH_4OH instead of NaOH.

(*b*) The nitric acid solution of Hg, Bi, Pb, Cu and Cd is almost neutralised cautiously with NaOH solution, till faintly acidic; boil and add excess of β-resorcylic acid solution with stirring to complete precipitation. Filter and wash once or twice with warm water.


Precipitate : Hg (white with yellowish tinge); dissolve in dilute HCl or HNO_3 and test by $SnCl_2$.
Filtrate : Bi, Pb, Cu and Cd; apply the procedure as in (*a*).

N.B.—In the above separation always fresh solutions of the phenolic acids should be used.

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Quanta-yield and "Chemismus" in Light Reaction.[1]

By J. Plotnikow.

Up to the present moment not a single case is known to us in which "non-absorbed" (*i.e.*, reflected or transmitted) light has been chemically active. Such a case is scarcely to be expected and therefore the photochemical absorption law of Grotthus-van't Hoff must be regarded as a fundamental law of photochemistry. Properly speaking it is only a special case of the general law of conservation of energy in so far as it here relates to the mutual action ("Wechselwirkung") between the chemical energy and the energy of radiation.

The amounts of substances photochemically transformed are proportional to the amounts of light absorbed and for the simplest case of a single photoactive component the equation of kinetic reaction in its differential form appears as

$$\frac{dM}{dt} = kA,$$

where M is the quantity of substance transformed (or formed), t the time, A the quantity of light absorbed, k the proportionality factor which can also be regarded as the velocity constant of the light-reaction. If we measure $\triangle M$, the small amount of substance changed in the correspondingly small but still measureable interval of time $\triangle t$, the coefficient of utilisation—one can also call it the photochemical yield—can be calculated from the above formula as

$$K = \triangle M / \triangle t A.$$

We can measure this "utilisation coefficient" or yield, which represents the number of gram-molecules changed photochemically

[1] Translated by Dr. P. C. Mitter.

by the light energy absorbed per unit of time and per calorie (or erg), either by direct measurement of $\triangle M$, $\triangle t$ and A, or by measuring the light-reaction velocity constant with the help of the integrated kinetic equation. The first way is relatively simple and takes a short time while the second, on the other hand, is very complicated in every respect. Inspite of this, one has to go the second way, as the first gives in the majority of cases values which have no real meaning. We shall explain this further. It is well known that the photochemical processes are of a very complicated character. They have very often a period of induction (see Curve 2, Fig. 1), are mostly accompanied by all sorts of dark-reactions (Curve 4), possess often an autocatalytic character (Curve 3), form substances which absorb thermically, *i.e.*, extinguish the chemically acting light and are subject to complicated light partition between several components (Plotnikow and Weber, *Z. Elektrochem.*, 1928, **34**, 316), or the reaction tends to an equilibrium, that is, a reverse reaction with its photoactive components opposes it and diminishes the velocity of the first, etc., etc. In many cases, several of the phenomena related above, occur simultaneously. All these distort the normal course of a light-reaction as can be seen distinctly from Fig. 1.

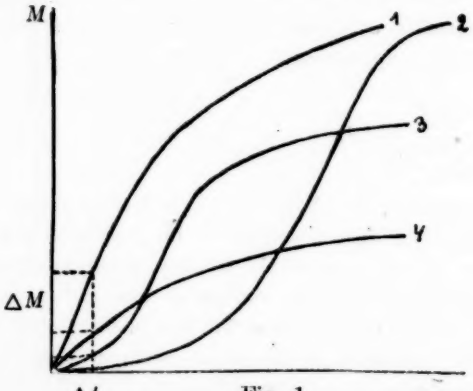

Fig. 1.

The determination of $\triangle M$ in the interval of time $\triangle t$ does not, therefore, in these cases, correspond to the normal course of the reaction which is free from all sorts of disturbances. Unfortunately the estimations of the yields are made in most cases without taking these circumstances into consideration and they cannot therefore possess any real photochemical value. From this follows the conclusion that one must

first of all thoroughly investigate every reaction kinetically, measure all side reactions, subtract them from the total and measure the yield from the course of the pure light-reaction obtained in this manner. In this connection, particular attention is to be paid to the dark-reactions which are to be eliminated according to the author's addition principle.

Let us assume that we have succeeded in freeing a light-reaction from all side reactions or in eliminating them by calculation, and arrived in this way at the course of the pure light-reaction. What should we do next? It is clear that we must determine the change of the light-reaction velocity constant with the wave-length as we shall have to deal mostly with complex absorption relations. Were these so simple that we had to deal only with strips of photochemical absorption, as for instance in the case of the bleaching of colouring matters thoroughly investigated photochemically by Lasareff (*Ann. Physik*, 1907. **24**, 661) and Zschodro (*J. Chim. Phys.*, 1929, **16**, 59), the reaction velocity would then be independent of the wave-length, because the velocity depends only on the absorbed light energy. Ordinarily, however, thermic absorption is associated with the photochemical absorption, giving the total absorption processes a very complicated form. Fig. 2 is a symbolic representation of these relations. The strips of photochemical absorption possess, as the experiments have shown (Plotnikow and Karshulin. *Z. Physik*, 1926, **36**, 271), mostly a very simple form with a single maximum. The possibility of occurrence of a number of maxima by the superposition of several strips of photochemical absorption is, however, not excluded. In these whole strips, the velocity is proportional to the energy absorbed and the proportionality coefficient is independent of the wave-length. But as we measure in practice not the photochemical but the total absorption, so, the proportionality coefficient must accordingly change with the wave-length.

If we succeed in measuring K for the pure photochemical absorption for any particular wave-length, we can, with the help of this value of K and the constant k_λ for any other wave-length λ for which the total absorption $c_\lambda = A_\lambda + B_\lambda$) calculate the photochemical absorption A_λ corresponding to this wave-length according to the equation $A = \frac{k_\lambda}{K} C_\lambda$. For this wave-length λ, the velocity $\frac{\triangle M_\lambda}{\triangle t} = K_\lambda C_\lambda$, the chemical action is, however, effected only through the

photochemically absorbed light (see Fig. 2) so that we must have $\frac{\triangle M\lambda}{\triangle t} = \lambda KA$.

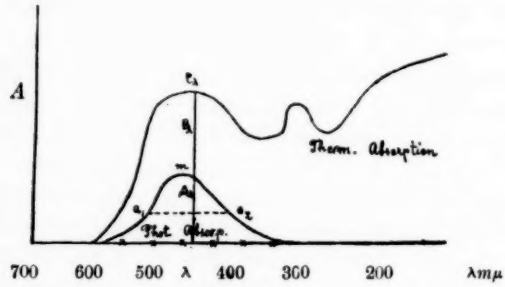

Fig. 2.

The above given relation for $A\lambda$ is obtained for these two equations. In this way the curve of the entire photochemical absorption can be reconstructed and the absorption can be measured quantitatively even in case of complicated absorption processes. It is not excluded, however, that the same could be quantitatively measured by other methods, as for instance by applying a method similar to that of Henri, which was employed for measuring the light absorption constant with the help of the light absorptions spectra (Plotnikow and Karshulin, *loc. cit.*).

We can also put the calculation of the yield in quanta forms *i.e.*, measure the number of molecules changed photochemically for one light quantum absorbed. For this, one has to calculate $A : h\nu$, the number of quanta $h\nu$ present in the absorbed energy A and to measure the number of molecules transformed with the help of the Avogadro-Loschmidt constant. The quanta-yield becomes in this case

$$\psi = \frac{Q\triangle M}{q\triangle t}$$

where Q is the Avogadro-Loschmidt number and q the number of absorbed light-quanta ($=A/h\nu$). The calculation of ψ can be further simplified if we take the ratio of gram-molecules transformed to the gram-molecules light-quanta $Qh\nu$ absorbed, as we can measure the change in gram-molecules ($\triangle M$) directly and calculate $Qh\nu$ from the photochemical tables of my book ("Photo-Chemische Versuchstechnik," 2nd Edition, 1928, pp. 327, 359).

As is well-known $Q = 6{\cdot}05 \times 10^{23}$ and $h = 6{\cdot}56 \times 10^{27}$ erg. sec., and the frequency ν has been calculated in the tables for every wave-

length. On dividing the values given there for $\nu \times 10^{12}$ by 10, one obtains the gram-molecular light-quanta energy in big calories (*loc. cit.*).

Let us assume that we have before us only photochemical absorption that is only the inner curve in Fig. 2 as is for instance the case in the experiments of Lasareff and Zschodro. The yield measured in terms of energy remain constant, independent of the wave-length. Not, however, the quanta yields because, for example, they must be different in two equal absorptions a_1 and a_2, as ν increases and thereby the value of ψ decreases. How is it then that by a different method of calculation one arrives at such an abnormal end-result? It is clear that this disagreement is due to some tacit assumption which is contradictory to the real facts. The assumption is that a light-quantum brings about the change only of a single molecule and that thereby the quantum transforms its energy completely into chemical energy. Both the assumptions which have hitherto been regarded as something axiomatic cannot correspond to the real facts and that on the following grounds.

As is well known, an atom or a molecule represents a complex dynamic structure, consisting of numerous electrons rotating round the nucleus in different orbits. When a light quantum falls into this complex it must produce the most diverse effects such as one can represent symbolically by Fig. 3.

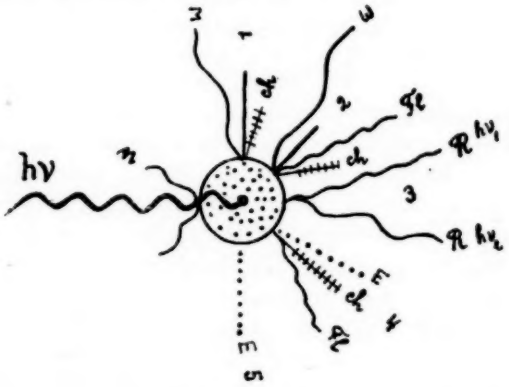

Fig. 3.

The energy $h\nu$ of the light-quantum can transform itself partly into heat radiation, kinetic energy of the molecules, (*i.e.*, heat)and chemical energy (case I). In case II, $h\nu$ would transform itself into

kinetic energy, heat radiation, chemical energy and fluorescence, *i.e.*, again into radiation of lesser energy. In case III, $h\nu$ would be transformed into two new radiations $h\nu_1$, and $h\nu_2$ both with smaller frequencies but the sum $h\nu_1 + h\nu_2 = h\nu$, the so-called Raman-effect, would remain constant. In case IV (the so-called photoelectric effect) free electrons, pronounced fluorescence and chemical action would appear accompanied by weak heat-effect. In case V, principally free electrons are formed as is the case for instance with very hard Röntgen rays. These electrons can, in their turn, give rise to chemical action through electronic impact. Case IV corresponds to the ultra-violet portion of the spectrum. The case III, the Raman-effect, appears in all substances. The case II corresponds to the action of the rays with large wave-length and case I to the action of the infra-red rays. Of course many other possibilities of combination are conceivable. Besides a portion of the radiation is scattered in a diffused manner.

The percentage ratio of the different forms of light energy distribution depends not only on the reacting wave-length but also to a large extent on the "Chemismus" *i.e.*, the chemical properties of each particular compound individually, the medium, the temperature, added catalysts and other active and inactive components. In very few exceptional cases, under quite definite conditions of experiment, can $h\nu$ be converted approximately completely in any one of the above given forms of energy. So, the method of representation of the primary stage of photochemical action as

$$M + h\nu = M' \text{ (activated)},$$

which has become so common in recent times, has neither a real nor a symbolical significance. Also the enormous divergences which are obtained as the results of experiments with regard to the assumption, that an $h\nu$ is transformed completely into chemical energy, need not make us wonder. What strikes one is, on the other hand, the fact that no correct conclusions had been hitherto drawn from the results of these experiments (*cf. Physikal. Chem.* (Oxford band), 1929, **120**; *Faraday Soc., Disc.*, **21**, Part 3, p. 63; Bhattacharya and Dhar, *Z. anorg. Chem.*, 1928, **169**, 381; Plotnikow, *Z. wiss. Phot.*, 1922, **21**, 134; 1923, **22**, 108; *Phot. Korr.*, 1927, **63**, 4; Plotnikow and Karschulin, *Z. Physik*, 1926, **36**, 271; 1926, **38**, 502; *Z. Elektrochem.*, 1927, **33**, 213).

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The Change of Viscosity of Sols and of Precipitating Concentrations of Electrolytes with their Purity and the Change of the Ratio of Precipitating Concentrations with the Temperature of Coagulation.

By V. Gore and N. R. Dhar.

In a recent communication (Dhar and Gore, *J. Indian Chem. Soc.*, 1929, **6**, 31) we have shown that the ratio of the precipitating concentrations of uni- and bi-valent and uni- and tri-valent ions with several hydroxide sols becomes less as the purity of the sols is increased. The same behaviour is also observed with the increase in temperature at which the coagulation is effected. We have extended our work to other sols and in this paper we are recording our results on the change of viscosity with the purity of ferric, stannic, ceric, zirconium, and thorium hydroxides, arsenious sulphide, antimony sulphide, cupric ferrocyanide, Prussian blue, uranium ferrocyanide, mastic and gamboge sols. We have also investigated the influence of temperature on the ratio of precipitation concentrations of uni- and bi-valent ions on some sols.

Ferric hydroxide sols.

A solution of Kahlbaum's ferric chloride was added to boiling water and a clear brownish red sol was obtained. The sol was kept in a parchment paper bag and was dialysed in hot water (80°-90°). As the dialysis progressed from time to time, a sufficient quantity of the sol was taken out and the purity, viscosity and ratio of the precipitating concentration were determined. The viscosity measurements were made in the same way as described previously (*Z. anorg. Chem.*, 1926, **152**, 393).

TABLE I.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

The day of the hot dialysis.	Conc. of the sol (Fe_2O_3 per litre).	Amt. of Cl per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of K_2SO_4 to coagulate.	Ratio of pptng. conc.	Viscosity at 30° (water = 0·00803).
2nd. A	1·48 g.	0·7139 g.	2·07	2·5 c.c. 2*N*	0·5 c.c. *N*/100	1·000	0·00814
3rd. B	3·60	0·1511	23·82	2·0 c.c. *N*/10	0·2 c.c. *N*/100	100	0·00833
6th. C	4·28	0·1329	32·20	0·6 c.c. *N*/10	0·5c.c. *N*/500	60	0·00847
8th. D	4·32	0·0465	90·80	0·2 c.c. *N*/10	0·4 c.c. *N*/500	25	0·00855
10th. E	4·32	0·03304	130·75	0·9 c.c. *N*/100	0·3 c.c. *N*/500	15	0·00938
11th. F	5·52	0·03800	167·20	0·4 c.c. *N*/100	0·2 c.c. *N*/500	10	0·00961
14th. G	5·18	Partly coagulated.		0·2 c.c. *N*/100	0·15 c.c. *N*/500	6·6	—

Stannic hydroxide sols.

Stannic hydroxide was precipitated by the action of ammonium hydroxide on stannic chloride solution. The precipitate on washing once or twice with water passes into a negatively charged clear sol, which was purified by hot dialysis.

TABLE II.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c. c.

The day of the hot dialysis.	Conc. of the sol (SnO_2 per litre).	Amt. of NH_3 per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of $BaCl_2$ to coagulate.	Ratio of the pptng. conc.	Viscosity at 30° (water = 0·00803).
2nd. A	18·24g.	1·0 g.	18·24	1·2 c.c. *N*	1·5 c.c. *N*/100	160	0·00863
3rd. B	18·24	0·6	30·40	0·5 c.c. 2*N*	1·0 c.c. *N*/100	100	0·00877
4th. C	18·24	0·4	45·6	1·5 c.c. *N*/5	0·9 c.c. *N*/100	35·5	0·01080
6th. D	22·92	0·2	113·6	0·7 c.c. *N*/5	0·7 c.c. *N*/100	20·0	0·01123
8th. E	5·96	0·03	198·66	0·6 c.c. *N*/100	1·0 c.c. *N*/1000	6	0·0572
10th. F	7·68	0·02	—	Coagulated itself.			

Ceric hydroxide sols.

30 Gm. of ceric ammonium nitrate were dissolved in 400 c. c. of hot water and filtered while hot into a parchment bag. The ceric

hydroxide sol thus obtained was purified by hot dialysis. The nitrate was estimated by colorimetric methods.

TABLE III.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

The day of the hot dilaysis.	Conc. of the sol CeO_2 per litre.	Amt. of nitrate per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of K_2SO_4 to coagulate.	Ratio of the pptng. conc.	Viscosity at 30°.
3rd. A	24·96g.	15·5g.	1·61	2 c.c. 2*N*	3·9 c.c. *N*/100	102·5	0·00842
6th. B	44·76	0·62	72·1	1 c.c. *N*/5	3·0 c.c. *N*/100	6	0·0110
10th. C	131·7	0·248	531	0·5 c.c. *N*/5	3·0 c.c. *N*/100	3·3	0·0226

Zirconium hydroxide sols.

33 Gm. of zirconium oxychloride were dissolved in 400 c. c. of hot water ; to this solution ammonia was added drop by drop until the precipitate first formed just dissolved. The sol was purified by hot dialysis.

TABLE IV.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c. c.

The day of the hot dialysis.	Conc. of the sol (ZrO_2 per litre.)	Amt. of Cl per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of K_2SO_4 to coagulate.	Ratio of the pptng. conc.	Viscosity at 30°.
	1st, preparation.						
A	12·64g.	0·7420g.	17·3	0·5 c.c. *N*/5	0·8 c.c. *N*/400	50	0·0413
	2nd. preparation.						
4th. A′	32·36	4·08	7·9	4 c.c. 2*N*	0·2 c.c. *N*/5	20	Very high.
5th. B′	28·40	3·27	8·7	0·6 c.c. *N*/5	0·1 c.c. *N*/5	6	,
7th. C′	A jelly was formed in the bag.						

Thorium hydroxide sols.

A solution of thorium chloride (Kahlbaum) was boiled for about half an hour to increase the hydrolysis and was subjected to hot dialysis.

TABLE V.

Volume = 5 c. c. Time = 1 hour. Sol taken = 1 c. c.

No. of the sol.	Conc. of the sol (ThO_2 per litre).	Amt. of Cl per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of K_2SO_4 to coagulate.	Ratio of the pptng. conc.	Viscosity at 30°.
A	14·12g.	1·029g.	13·73	—	0·4 c.c. $N/5$	>400	0·00839
B	12·96	0·6989	18·50	2·3 c.c. $4N$	2·85 c.c.$N/100$	322·8	0·00842
C	0·92	0·0050	184·7	·04 c.c $N/100$	0·1 c.c.$N/500$	20	0·00957
D	Partly coagulated.			0·01 c.c. $N/100$	0·01. c.c.$N/500$	5	—

In the cases of ferric, stannic, ceric, zirconium and thorium hydroxide sols, the viscosity increases steadily with the purity. These results strongly support our view that as the electric charge decreases the viscosity increases. As the sol becomes purer and purer, the adsorbed electrolyte becomes less and the charge decreases. Along with the decrease of the charge the viscosity of the hydroxide sols markedly increased.

The above results show that starting with a sol which is not pure, and which contains appreciable amounts of hydrochloric acid in the adsorbed condition, the hydrochloric acid is removed steadily by hot dialysis and the sol becomes purer and purer, and requires smaller and smaller quantities of electrolyte for coagulation. When the sols become very pure and the amount of adsorbed electrolyte is extremely small, the viscosity is enormously increased though the concentration of the sol remains practically constant.

In order to strengthen our view that less the charge, the greater is the viscosity, we have carried on the following experiments. Highly pure and viscous sols of ferric, stannic and zirconium hydroxides were shaken with definite amounts of ferric chloride, zirconium oxychloride and ammonium hydroxide. These electrolytes act as

peptisers for the above sols. The following are the experimental results.

TABLE VI.

Ferric hydroxide sols.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

Amt. of sol taken.	Amt. of $FeCl_3$ solution to peptise (c.c.).	Conc. of the sol (Fe_2O_3 per litre).	Amt. of Cl per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of K_2SO_4 to coagulate.	Ratio of the pptng. conc.	Viscosity at 30°.
50 c.c. of E sol.	5	5·48g.	0·2123g.	25·6	1·7 c.c. 2*N*	1·2 c.c. *N*/100	283·3	0·00837
E sol.	0	4·32	0·03304	130·75	0·9 c.c. *N*/100	0·3c.c. *N*/500	15	0·00938
50 c.c. of F sol.	10	8·62	0·3713	23·2	1·5 c.c. 2/*N*	1·4 c.c. *N*/100	214·2	0·00884
F sol.	0	5·52	0·0330	167·2	0·4 c.c. *N*/100	0·2 c.c. *N*/500	10	0·00961
19 c.c. of G sol.	10	11·02	2·501	4·3	2·2c.c. 2*N*	1·7 c.c. *N*/100	258·8	0·00869
G sol.	—	5·18	—	—	Partly coagulated and highly viscous.			

TABLE VII.

Stannic hydroxide sols.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

Amt. of sol taken.	Amt. of NH_4OH (4·26*N*)	Amt. of KCl to coagulate.	Amt. of $BaCl_2$ coagulate.	Ratio of the pptng conc.	Viscosity at 30°
20 c.c. of E sol.	1 c.c.	3·5 c.c. *N*/10	0·45 c.c. *N*/100	77·7	0·00911
E sol.	0	0·6 c.c. *N*/100	1·0 c.c. *N*/1000	6	0·0572

TABLE VIII.

Zirconium hydroxide sols.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

Amt. of sols taken.	Amt. of Zr-oxychloride soln (c.c.).	Conc. of the sol (ZrO_2 per litre.)	Amt. of Cl per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of K_2SO_4 to coagulate.	Ratio of the pptng. conc.	Viscosity at 30°.
40 c.c. of B sol, 1st preparation.	10	10·76g.	0·6273g.	17·1	0·5 c.c. *N*	1·8 c.c. *N*/400	111	0·0125
B sol, 1st preparation.	0	12·64	—	—	—	—	50	0·0413

The above results show that the highly purified sols of ferric, stannic and zirconium hydroxides, which are highly viscous, can become much less viscous when their electric charges and stability are increased by the adsorption of the peptising electrolytes. Hence we have been able to establish definitely that by starting with impure sols the viscosity goes on increasing as the sol becomes more and more unstable and pure. On the other hand, starting with highly pure and viscous sols the viscosity can be decreased by increasing their charge and stability consequent upon the adsorption of the peptising electrolytes. Hence the relation between the stability and the viscosity appears to be a reversible phenomenon and can be established from both sides.

We have observed an interesting fact in the case of stannic hydroxide sol. The coagulum in the case of sols which were not specially pure and not highly viscous appears white whilst the coagulum obtained in the coagulation of the highly purified and viscous sols appeared almost transparent and far less white. This observation also proves the fact that with increased purity there is more hydration of the particles and hence the whiteness decreases.

In the case of sols of arsenious sulphide, antimony sulphide, Prussian blue, copper ferrocyanide, uranium ferrocyanides, mastic, gamboge, etc., no definite relation regarding the viscosity and purity could be established because these sols are steadily hydrolysed. But in the cases of antimony and arsenious sulphide sols it is seen that,

on the addition of hydrogen sulphide to both these sols, the precipitating concentration is appreciably increased. These results also prove that as the stability of the sol is increased by the adsorption of the peptising electrolytes, the ratio of the amounts of mono- and bi-valent ions, necessary for coagulation, also increases though in a much less marked manner than in the case of hydroxide sols.

Arsenious sulphide sols.

The sol was prepared as usual from As_2O_3 and then was subjected to dialysis at the ordinary temperature.

TABLE IX.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

Sol.	Conc. of the sol. (As_2S_3 per litre).	Amt. of H_2S per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of $BaCl_2$ to coagulate.	Ratio of pptng. conc.
A	2·57 g.	0·17 g.	15·1	2·1 c.c. *N*/5	0·7 c.c. N/100	60
B	2·38	0·17	14·0	2·4 c.c. *N*/5	0·8 c.c. *N*/100	60
B peptised with H_2S	1·98	0·425	4·65	3·0 c.c. *N*/5	0·8 c.c. *N*/100	75
C	3·735	0·17	21·9	2·7 c.c. N/5	0·9 c.c. *N*/100	60

Antimony sulphide sols.

The sol was prepared from potassium antimony tartrate. The amount of potassium sulphate and hence potassium tartrate was found out by evaporating the filtrate after coagulating the sol with hydrochloric acid, and drying with concentrated sulphuric acid in a platinum crucible.

TABLE X.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

No. of the sol.	Conc. of the sol (Sb_2S_3 per litre).	Amt. of K_2SO_4 per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of $BaCl_2$ to coagulate.	Ratio of pptng. conc.
A	5·45 g.	0·55 g.	9·09	0·9 c.c. *N*/5	0·8 c.c. *N*/100	22·5
B	5·53	0·55	9·10	0·86 c.c. *N*/5	0·75 c.c. *N*/100	22·2
C	6·325	0·55	11·40	0·85 c.c. *N*/5	0·75 c.c. *N*/100	22·2
C peptised with H_2S	7·6	0·60	12·6	0·9 c.c. *N*/5	0·5 c.c. *N*/100	36·0

Uranium ferrocyanide sols.

Dilute solutions of uranium nitrate and potassium ferrocyanide (excess) were mixed. The sol thus obtained was subjected to dialysis at the ordinary temperature, because by hot dialysis the uranium ferrocyanide sol is decomposed.

TABLE XI.

Volume=5 c.c. Time=1 hour. Sol taken=1 c.c.

Sol.	Conc. of the sol (U-ferrocyanide per litre).	Amt. of $K_4Fe(CN)_6$ per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of $BaCl_2$ to coagulate.	Ratio of the pptng. conc.	Viscosity at 30°.
A	3·72 g.	2·54 g.	1·49	2·3 c.c. *N*	0·6 c.c. *N*/10	38·3	0·00868
B	2·42	1·47	1·65	1·0 c.c. *N*	0·3 c.c. *N*/10	33·3	0·00849
C	1·66	1·105	1·50	0·8 c.c. *N*	0·2 c.c. *N*/10	40	0·00837
D	1·44	0·929	1·50	0·8 c.c. *N*	0·2 c.c. *N*/10	40	0·00830
E	0·86	0·5892	1·49	0·8 c.c. *N*	0·2 c.c. *N*/10	40	0·00822

Copper ferrocyanide sol.

Dilute solutions of copper sulphate and potassium ferrocyanide (excess) were mixed. The sol thus obtained was subjected to dialysis at the ordinary temperature.

TABLE XII.

Volume=5 c.c. Time=1 hour. Sol taken=1 c.c.

Sol.	Conc. of the sol (Cu-ferrocyanide per litre).	Amt. of $K_4Fe(CN)_6$ per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of $BaCl_2$ to coagulate.	Ratio of the pptng conc.
A	7·82 g.	22·09 g.	0·35	2·0 c.c. *N*/100	1·0 c.c. *N*/100	2
B	11·16	11·78	0·99	0·5 c.c. *N*/5	1·4 c.c. *N*/100	8·3

Prussian blue.

Dilute solutions of ferric chloride and potassium ferrocyanide (excess) were mixed. In order to help the peptisation a small amount of oxalic acid was used. The sol thus obtained was subjected to dialysis at the ordinary temperature.

TABLE XIII.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

Sol.	Conc. of the sol (Fe_2O_3 per litre).	Amt. of $K_4Fe(CN)_6$ per litre.	Purity.	Amt. of KCl to coagulate.	Amt. of $BaCl_2$ to coagulate.	Ratio of the ppt. ng. conc.	Viscosity at 30°.
A	16·46 g.	17·82 g.	0·92	0·5 c.c. 2*N*	0·5 c.c. *N*	3	0·01013
B	7·48	15·26	0·37	0·2 c.c. *N*/5	1·5 c.c. *N*/100	2·6	0·01267
C	7·52	19·89	0·48	0·2 c.c. *N*/5	1·5 c.c. *N*/100	2·6	0·01144
D	4·24	12·52	0·33	0·2 c.c. *N*/5	1·5 c.c. *N*/100	2·6	—

Mastic sols.

About 10 gm. of mastic were dissolved in 200 c.c. of alcohol. The solution was poured into distilled water drop by drop and stirred well. The sol thus obtained was subjected to dialysis at the ordinary temperature.

TABLE XIV.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

Sol.	Conc. of the sol per litre.	Amt. of KCl to coagulate.	Amt. of $BaCl_2$ to coagulate.	Ratio of the ppting. conc.	Viscosity at 30°.
Not dialysed ...	1·96	1·4 c.c. 2*N*	1·8 c.c. *N*/10	15·5	0·01012 (high viscosity due to alcohol.)
Dialysed ...					
A	1·94	1·4 c.c. 2*N*	1·8 c.c. *N*/10	15·5	0·00826
B	1·80	1·4 c.c. 2*N*	1·8 c.c. *N*/10	15·5	0·00818

Gamboge sols.

5 Gm. of powdered gamboge dissolved in alcohol were poured drop by drop into 500 c.c. of water. The sol thus obtained was subjected to dialysis at the ordinary temperature.

TABLE XV.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

Sol.	Conc. of the sol per litre.	Amt. of KCl to coagulate.	Amt. of $BaCl_2$ to coagulate.	Ratio of the ppting. conc.	Viscosity at 30°.
A	2·84 g.	2·3 c.c. *N*	0·7 c.c. *N*/10	32·8	0·00835
B	3·70	2·2 c.c. *N*	0·7 c.c. *N*/10	31·4	0·00829
C	3·56	2·2 c.c. *N*	0·7 c.c. *N*/10	31·4	0·00834

The coagulation of some of hydroxide sols are carried on at 60° in order to find out the influence of temperature on the ratio of the precipitating concentration of mono- and bi-valent ions. The experimental results are recorded in the following tables.

TABLE XVI.

Ferric hydroxide sols.

Volume = 5 c.c. Time = 1 hour. Sol taken = 1 c.c.

Sol.	At 30°		Ratio of the pptng. conc. at 30° (*a*)	At 60°		Ratio of the pptng. conc. at 60°. (*b*)	*a* : *b*
	Amt. of KCl to coagulate.	Amt. of K_2SO_4 to coagulate.		Amt. of KCl to coagulate.	Amt. of K_2SO_4 to coagulate.		
Sol A	2·5 c.c. *2N*	0·5 c.c. *N*/100	1000	1·4 c.c. *2N*	0·4 c.c. *N*/100	700	1 : 0·7
Sol B	2·0 c.c. *N*/10	0·2 c.c. *N*/100	100	0·7 c.c. *N*/5	1·0 c.c. *N*/500	70	1 : 0·7
Sol D	0·2 c.c. *N*/10	0·4 c.c. *N*/500	25	0·05 c.c. *N*/5	0·3 c.c. *N*/500	16·6	1 : 0·66
Sol E + 5 c.c. $FeCl_3$	1·7 c.c. *2N*	1·2 c.c. *N*/100	283·3	2·4 c.c. *N*	1·2 c.c. *N*/100	200	1 : 0·705
Sol F + 5 c.c. $FeCl_3$	1·5 c.c. *2N*	1·4 c.c. *N*/100	214·2	2·1 c.c. *N*	1·4 c.c. *N*/100	150	1 : 0·7002

TABLE XVII.

Zirconium hydroxide sols.

Sol.	At 30°		Ratio of the pptng. conc. at 30° (*a*)	At 60°		Ratio of the pptng. conc. at 60° (*b*)	*a* : *b*.
	Amt. of KCl to coagulate.	Amt. of K_2SO_4 to coagulate.		Amt. of KCl to coagulate.	Amt. of K_2SO_4 to coagulate		
Sol A	0·4 c.c. *2N*	0·2 c.c. *N*/5	20	0·3 c.c. *N*	0·09 c.c. *N*/5	16·6	1 : 0·33
Sol B	0·6 c.c. *N*/5	0·1 c.c. *N*/5	6	0·5 c.c. *N*/5	2·0 c.c. *N*/100	5	1 : 0·833

TABLE XVIII.

Ceric hydroxide sols.

Sol.	At 30°: Amt. of KCl to coagulate.	At 30°: Amt. of K_2SO_4 to coagulate.	Ratio of the pptng conc. at 30° (*a*)	At 60°: Amt. of KCl to coagulate.	At 60°: Amt. of K_2SO_4 to coagulate.	Ratio of the pptng. conc. at 60° (*b*)	*a* : *b*.
Sol A	2·0 c.c. *2N*	3·9 c.c. *N*/100	102·5	1·8 c.c. *N*	3·6 c.c. *N*/100	50	1 : 0·49
Sol B	1·0 c.c. *N*/5	3·0 c.c. *N*/100	6	0·4 c.c. *N*/5	2·9 c.c. *N*/100	3·1	1 : 0·5

TABLE XIX.

Stannic hydroxide sols.

Sol.	At 30°: Amt. of KCl to coagulate.	At 30°: Amt. of $BaCl_2$ to coagulate.	Ratio of the pptng. conc. at 30° (*a*)	At 60°: Amt. of KCl to coagulate.	At 60°: Amt. of $BaCl_2$ to coagulate.	Ratio of the pptng. conc. at 60° (*b*)	*a* : *b*
Sol A	1·2 c.c. *2N*	1·5 c.c. *N*/100	160	1·2 c.c. *N*	0·8 c.c. *N*/100	150	1 : 0·9
Sol B	0·5 c.c. *2N*	1·0 c.c. *N*/100	100	0·75 c.c. *N*	0·8 c.c. *N*/100	93·75	1 : 0·9
Sol C	1·5 c.c. *N*/5	0·9 c.c. *N*/100	35·5	0·70 c.c. *N*/5	0·6 c.c. *N*/100	23·3	1 : 0·7

The above experimental results show that as the temperature is increased the ratio of the precipitation concentrations becomes less.

One thing, however, comes out prominently namely that these ratios change in such a way that the ratio of the precipitation concentrations at 30° to 60° is equal to constant, irrespective of the purity of the sol.

Summary.

1. The experimental results obtained in the viscosity measurements with sols of ferric, stannic, ceric, zirconium and thorium hydroxides of different degrees of purity show that the viscosity of these sols increases steadily with their purity, even when their concentrations are practically constant.

2. When these hydroxide sols are very pure and unstable and the amount of adsorbed electrolyte is very small, their viscosities are enormously increased.

3. Experimental results show that highly purified sols of ferric, stannic and zirconium hydroxides becom less viscous when their electric charges and stability are increased by the adsorption of peptising electrolytes.

4. The coagulum obtained from a sol of stannic hydroxide which is not specially pure and is not lightly viscous, is white; whilst the coagulum with a highly purified and viscous sol of stannic hydroxide is almost transparent and far less white.

5. Hence it appears that increased purity of a sol is associated with greater hydration and greater viscosity. These experimental results strengthen our view that the less the charge on a sol, the greater its viscosity.

6. Experimental results obtained with all the hydroxide sols show that the ratio of the precipitating concentrations of uni- and bi-valent ions decreases as the purity and the viscosity of the sols increases.

7. No definite relation regarding the viscosity and purity of the sols could be established with sols of arsenious sulphide, antimony sulphide, Prussian blue, cupric ferrocyanide, uranium ferrocyanide, mastic and gamboge, since all these sols are steadily hydrolysed on dialysis.

8. On increasing the temperature of coagulation, the ratio of the precipitating concentrations of uni- and bi-valent ions with ferric, ceric, and stannic hydroxide sols become less; but these ratios change in such a way that the ratio of the values at 30° and 60° remains constant irrespective of the purity of the sols.

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Studies in Silicic Acid Gels. Part I. The Time of Setting of Gels.

By Mata Prasad and R. R. Hattiangadi.

Fleming (*Z. Physik*, 1902, **41**, 427) prepared the silicic acid gel by mixing a solution of sodium silicate with different concentrations of sulphuric and nitric acids and found that the time of set of the gel was a minimum when the mixtures of the silicate and the acids were slightly alkaline. He considered the gel as set when the vessel containing the mixtures could be inverted without the gel flowing out.

Holmes (*J. Phys. Chem.*, 1918, **22**, 510) prepared the gel by mixing solutions of sodium silicate with solutions of phosphoric, acetic, citric and tartaric acids of varying concentrations and found that the time of set of the gel was a minimum at two concentrations of the acids, one being very low and the other very high. Fells and Firth (*J. Phys. Chem.*, 1925, **29**, 241) using solutions of hydrochloric acid and sodium silicate found that the gel set in minimum time when the mixture was just alkaline and when the concentration of the acid was 10*N*.

Bhatnagar and Mathur (*Kolloid Z.*, 1922, **30**, 368) were able to prepare very good gels by mixing solutions of ammonium acetate and sodium silicate. In the following, a systematic study of the formation of silicic acid gels by the latter method has been made, when the concentrations of the solutions of ammonium acetate and sodium silicate are gradually varied, and an attempt has been made to obtain some definite knowledge of the factors which control the time of setting of the gel.

Experimental.

Preparation of Solutions.

A large quantity of Merck's dry sodium silicate (E. P. crystals) was kept in contact with distilled water for a period of two or three days. When a clear supernatant liquid was obtained,

it was twice filtered and stocked in a well-stoppered flask. Such a solution could keep undecomposed for a period of over three months. The strength of the sodium silicate was determined by estimating the silica content of this solution, and the other solutions required for the investigation were prepared by diluting the above. The strength of the different solutions has been expressed in grams of SiO_2 per 100 c.c.

Gels with Neutral Ammonium Acetate.

The neutral ammonium acetate obtained from British Drug House, Ltd. on analysis, gave ammonia and acetic acid in the proportion required by theory. The times of setting of the various gels were measured by Fleming's method (*loc. cit.*) and the results obtained are described in Tables I-VII.

TABLE I.

Concentration of SiO_2=0·493 per cent. Reaction alkaline.

Concentration of NH_4Ac :	8	10	21 per cent.
Time of setting (mins.) :	12	5	2 Ppt.

TABLE II.

Concentration of SiO_2=0·985 per cent. Reaction alkaline.

Concentration of NH_4Ac :	5	6	8	10	21 per cent.
Time of setting :	11′30″	4′50″	3′30″	1′20″ (No firm gel)	Ppt.

In the above two cases where the concentration of silica is comparatively low, the gels formed are very flimsy and a little tilting of the test tube disturbs the gel structure and it begins to synerise.

TABLE III.

Concentration of SiO_2 = 1·97 per cent. Reaction alkaline.

Concentration of NH_4Ac :	4	5	6	8	10	21 per cent.
Time of setting :	20′	4′30″	2′	55″	10″	Inst. ppt.

TABLE IV.

Concentration of SiO_2=3·3 per cent. Reaction alkaline.

Concentration of NH_4Ac :	4	4½	5	6	8	10	21 per cent.
Time of setting :	50′	12′	5′10″	1′40″	35″	Inst. ppt.	Flocks.

TABLE V.

Concentration of SiO_2=3·94 per cent. Reaction alkaline.

Concentration of NH_4Ac :	4	4½	5	6	8	10 per cent.
Time of setting :	72′	18′	6′50″	2′	40″	Inst. gel.

TABLE VI.

Concentration of SiO_2=4·92 per cent. Reaction alkaline.

Concentration of NH_4Ac :	2·5	4	5	6	8	10 per cent.
Time of setting :	25 days	5 hrs. 10′	12′	2′30″	45″	Inst. ppt.

TABLE VII.

Concentration of SiO_2=6·6 per cent. Reaction alkaline.

Concentration NH_4Ac :	2·5	5	6	8	10 per cent.
Time of setting :	More than 25 days	45′	4′40″	50″	1″

The time of setting of these gels decreases as the concentration of ammonium acetate is increased up to a certain concentration only. Higher concentrations give no gels but flocculent precipitates. Also all the gels are alkaline to litmus and no minimum value of the time of set is observed as in the case of gels obtained from sodium silicate and acids.

But the behaviour of acidic ammonium acetate on the time of setting of silicic acid gels has been found to be different from the neutral one.

Gels with Acidic Ammonium Acetate.

A sample of ammonium acetate which was acidic was found to contain about 30 per cent. free acetic acid.

Equal volumes of this ammonium acetate were mixed with solutions of sodium silicate of different strengths and the time of setting was measured in the first instance by Fleming's method.

It was, however, observed in the case of these and the foregoing experiments that the method of measuring the time of set was not quite satisfactory as the gelling substance had to be frequently disturbed.

The criterion of setting of a gel, defined as a body which has a form or shape and is solid-like in appearance, should be the attainment of that form or shape, which occurs when its elasticity reaches a specific value. Hatschek (*Kolloid Z.*, 1926, **39**, 300) from a study of the shear moduli of sols and emulsions has shown that their elasticity is directly related to their viscosity. The viscosity of a suspension is known to depend upon the number of particles, their electric charge, degree of hydration and their specific nature.

Light scattered by any disperse system depends upon the size of the particles and the degree of dispersity. If a system is, therefore, undergoing a change in hydration and dispersity, scattering of light will change in the same way as the viscosity and hence its elasticity. It appears, therefore, that the method of scattering of light can be used as a correct criterion for determining the time of setting of the gel. This will have a further advantage of indicating the changes in the condition of the gel particles during the process of gelation and on changes in the silica content of the mixture.

Fells and Firth (*Trans. Faraday Soc.*, 1627, **23**, 623) suggested that the setting point of the gel should be that at which the pressure required to blow or suspend a bubble of air or of mercury or of chloroform coloured with iodine, through the gel-forming mixture reaches a maximum value. In this method the gel-forming mixtures are disturbed, whereby the setting process is considerably altered. The method of scattering of light, pointed out above, obviates this difficulty.

The method involving the variation in the intensity of the scattered light has also been used by Mardles (*Trans. Faraday Soc.*, 1923, **18**, 318) in the study of the sol-gel transformation of gels of cellulose

acetate. Arisz (*Kolloidchem. Beihefte*, 1915, **7**, 14) working with glycerol sols of gelatine also employed the same method and measured the intensity of the scattered light by a photographic method.

In the present investigation light from a lamp burning at 230 volts and 1·03 amps. was focussed for a parallel beam by a condenser of a long focal length. The parallel beam was then allowed to pass through a cell containing water to remove most of the heat rays and ultra-violet rays. This was then allowed to fall on a rectangular cell made of optically correct glass, containing the gel-forming mixture. The intensity of transmitted light was measured by means of a linear thermopile attached to a Broca galvanometer. The deflection of the galvanometer was measured on a scale placed at about one meter from it. The current passing through the lamp was adjusted to the same value, at each observation by means of a variable resistance, and the distance between the light source and the various cells was kept fixed throughout the whole investigation.

Equal volumes of ammonium acetate and sodium silicate were mixed thoroughly in a test-tube and transferred to the optical cell. The stop-watch was simultaneously started and the deflection of the galvanometer was measured at regular intervals of time. The results obtained are given in the following tables in which the symbols used represent: –

T = time after mixing the solutions, in minutes ;

D = deflection differences ($D_i - D_t$, where D_i is the initial and D_t the deflection at time t), in mms.

In all the mixtures examined, the concentration of ammonium acetate used was more than the equivalent quantity of the sodium silicate solution used.

TABLE VIII.

Concentration of SiO_2=2 per cent.

Concentrations of ammonium acetate.

4 per cent.		6 per cent.		8 per cent.	
T.	*D*.	*T*.	*D*.	*T*.	*D*.
0·5	0	0·5	0	1	0
1·5	0·5	1	5	2	0
3	2·5	1·5	11	5	1
5	6·5	2	18	7	1·5

TABLE VIII.—(*continued*)

T.	*D.*	*T.*	*D.*	*T.*	*D.*
6	11	2·5	23	10	4·5
7	13	3	24·5	12	8
8	14·5	3·5	25·5	14	11
9	16·5	4	25·5	17	13·5
10	17·5	4·5	25·5	19	15
12	18·5	—	—	20	15
15	18·5	—	—	21	15

TABLE IX.

Concentration of SiO_2=3 per cent.

Concentrations of ammonium acetate.

4 per cent.		5 per cent.		6 per cent.		12 per cent.	
T.	*D.*	*T.*	*D.*	*T.*	*D.*	T.	*D.*
1	0	0·25	0	0·25	0	1	0
4	3	1	2	1	10	2	1
6	7	1·5	4	1·5	20	2·5	4
8	12	2	9	2	26	3	7
10	16	2·5	13	2·5	27	5	15
12	19	3	16	3	27·5	7	19
14	20·5	4	21	4	28	9	21
16	21	5·5	26			10	22
20	22	6	26			11	22

TABLE X.

Concentration of SiO_2=4 per cent.

Concentrations of ammonium acetate.

4 per cent.		5 per cent.		6 per cent.		18 per cent.		20 per cent.	
T.	*D.*	*T.*	*D.*	*T.*	*D.*	*T.*	*D.*	*T.*	*D.*
1	0	1	0	0·25	0	1	0	1	0
2	0	1·5	2	0·75	10	2	0	2	0
5	0·5	2	5	1	18·5	4	3·5	5	1·5
10	3·5	2·5	9·5	1·5	28·5	6	8·5	10	3
15	8·5	3	15	2	33·5	8	13·5	16	10·5
17	10·5	4	21	3	36	10	16·5	20	14
25	20	6	27	3·5	36	12	16·5	23	15
30	24·5	8	28·5					28	15·5
40	27·5								

It will be seen from these tables that in each case the deflection of the galvanometer decreases as the time increases, at first rapidly and then slowly and more slowly until it reaches an almost constant value. These results have been plotted with deflection as ordinates against time as abscissa and typical curves are shown in Fig. 1. The

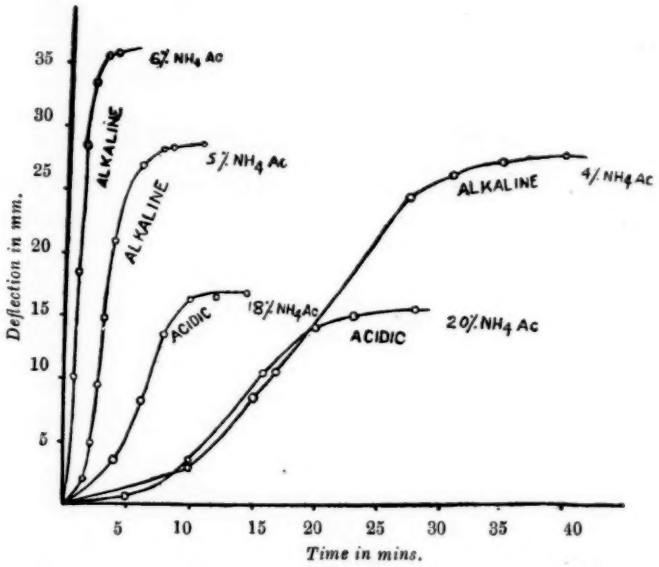

Fig. 1.

curves are sometimes sigmoid in shape there being a point of inflexion in the curve, after which there is a steady decline in the rate of change and point to the auto-catalytic nature of the reaction. The time when the deflection has become almost constant, *i.e.*, when the curve shows a tendency of running parallel to the time-axis, is read from the curve and taken as the time of setting of the gel.

These times of setting have been compared with those obtained by Fleming's method under similar conditions and are shown in the following tables. The reaction of these mixtures towards litmus has also been given in the last columns of these tables.

TABLE XI.

Concentration of SiO_2=2 per cent.

Conc. of NH_4Ac.	Time (Fleming's method).	Time (Optical method).	Reaction.
4 per cent.	7′	10′	Alkaline
5	2′40″	6′30″	,,
6	1′45″	3	,,
8	12′30″	18′	Acidic
10	90′	—	,,

TABLE XII.

Concentration of SiO_2=3 per cent.

Conc. of NH_4Ac.	Time (Fleming's method).	Time (Optical method.)	Reaction.
4 per cent.	9′30″	14′	Alkaline.
5	2′30″	5′30″	,,
6	1′	2′	,,
	0′25″		,,
10	0′25″	1′	...
12	5′	8′	Acidic.
16	60′	—	Acidic.

TABLE XIII.

Concentration of SiO_2=4 per cent.

Conc. of NH_4Ac.	Time (Fleming's method).	Time (Optical method).	Reaction.
4 per cent.	22′30″	35′	Alkaline.
5	3′	7′	,,
6	1′	2′	,,
8	10″	—	—
18	5′	9′	Acidic.
20	19′	24′	,,

The foregoing results show that the time of setting of the gel obtained by the optical method is always higher than that obtained by Fleming's method. This is, as was expected, as the latter method depends only upon the attainment of a certain viscosity by the mixture. As the gel begins to set, the viscosity of the mixture increases continuously until after some time it reaches a sufficiently high value to prevent the flowing out of the gel. At this point, however, the viscosity may not have reached its maximum value, as the size of the particles which contributes a lot to viscosity, still continues to

increase. Bachmann (*Z. anorg. Chem.*, 1911, **73**, 125) in an ultramicroscopic study of the structure of the jellies observed that the size of the particles increased during the ageing of the gel, and for systems of low concentrations, there was a gradual formation of separate flocculent particles or aggregates of sub-microns.

It will be further seen from the Tables (XI-XIII) that the time of setting of the gels depends both upon the concentration of silica and ammonium acetate. With a particular solution of sodium silicate and increasing concentrations of ammonium acetate, the time of set of the gels varies as shown in Fig. 2. On plotting log C against log T, C being the concentration of ammonium acetate and T the time of set of the gel, two intersecting straight lines are obtained. The equation to the original curve can, therefore, be written as

$$(t-ac^{n})(t-\beta c^{-m}) = 0$$

where a, β, n and m are constants.

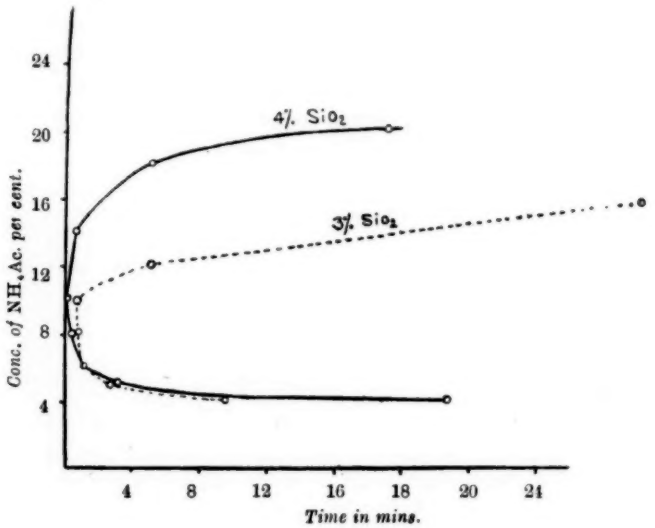

Fig. 2.

All mixtures set in a minimum time when they are slightly alkaline or neutral to litmus and the value of this minimum time is smaller, the greater is the silica content of the mixtures (*cf.* Flem-

ing, Fells and Firth). Highly alkaline and highly acidic mixtures take a long time to set.

The behaviour of the acidic ammonium acetate is different from that of the neutral one in that the former gives a minimum in the concentration-time of setting curves. Also, the reaction of all the gels obtained from the neutral ammonium acetate is alkaline but the acid one gives alkaline, neutral, or acid reaction depending upon the concentration of the ammonium acetate used. This indicates that the peculiar behaviour of acidic ammonium acetate is due to the presence of free acetic acid in it and that the variation in the time of setting depends upon the H- and OH-ion concentration of the mixtures.

Further examination of the gels obtained from acidic ammonium acetate showed that they differed in appearance from each other according as they were prepared from high or low concentrations of ammonium acetate. Differences in the structure of gels prepered from widely different concentrations, have been observed by Hardy (*J. Phys. Chem.*, 1900, **4**, 254) in systems of agar in water and gelatine in aqueous alcohol. The gels obtained in the present investigation can be classified into two types: (*a*) those which appear a bit opaque in transmitted light, (*b*) those which are transparent. The differences in the optical properties of these gels can be seen from the following results taken from Tables VIII-X.

TABLE XIV.

Absorption of Light in Terms of Galvanometer Deflection when the Gels set.

Conc. of NH_4Ac.	Concentration of silica.		
	2 per cent.	3 per cent.	4 per cent.
4 per cent.	18·5 mm.	22 mm.	27·5 mm.
5	—	27	28·5
8	15	—	—
12	—	22	—
18	—	—	16·5
20	—	—	15·5

Also, by reflected light (*a*) type gels appear more bluish than the (*b*) type ones.

It will be seen from the above table and Tables XI-XIII that mixtures which are even slightly acidic are more transparent than the alkaline ones. It seems, therefore, that the influence of the medium is an important factor in determining the transparency of the gels. The transparency of a disperse system depends upon the degree of dispersion and hence it appears that large aggregates are formed in alkaline mixtures than in acidic ones. The inference that the molecular aggregates formed in the gels from acidic mixtures are comparatively smaller than those from the alkaline ones, is similar to the observation of Linder and Picton (*J. Chem. Soc.*, 1892, **61**, 154), who found that no Tyndall-cone is shown by the undialysed sol of silicic acid in the presence of large concentrations of hydrochloric acid and concluded that molecular aggregates of sufficient size to scatter light, are not formed in these mixtures.

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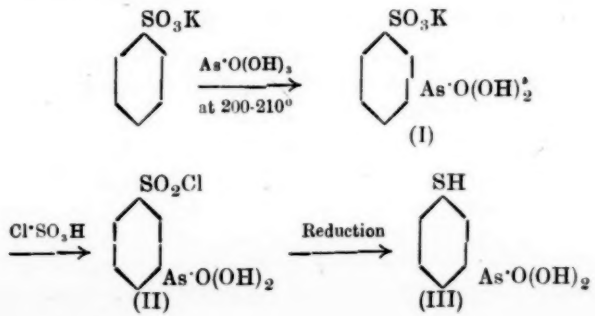
Synthesis of 4 : 4′-Dithiolarsenobenzene.

By S. Krishna and Radha Krishna.

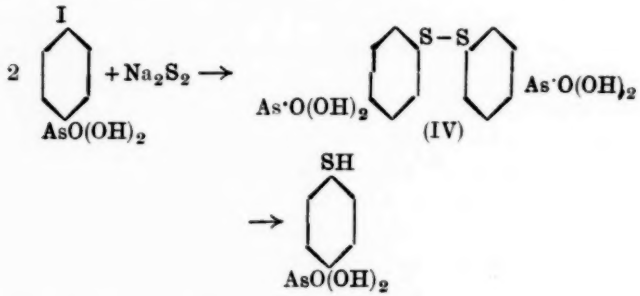
While studying the therapeutic value of azo-dyestuffs, Ehrlich found that the compounds containing amino- and hydroxyl-groups in the *ortho*-position were the most active in destroying trypanosomes. (Ehrlich and Hata, "Experimental Chemotherapy in Spirilloses." 1911, p. 18). With this object in view he prepared, the now famous salvarsan for treatment of diseases of the syphilitic origin, but found that there was one serious objection to the use of salvarsan in that it got readily oxidised into a highly poisonous substance and that its aqueous solutions were distinctly acidic and had to be exactly neutralised with alkali just before intravenous injection. Accordingly, Lucius and Bruning (D.R.-P. 245756) prepared neosalvarsan, a soluble salt free from the above drawbacks.

A large number of organo-metallic compounds of arsenic are known but no attempts have so far been made to prepare the thiol-analogues of salvarsan or neosalvarsan. The only effort in this direction was made by Hewitt, King and Murch (*J. Chem. Soc.*, 1926, **129**, 1359) who unsuccessfully attempted to prepare such compounds. The present work describes the preparation of certain arsenic compounds containing thiol-residues in the ring. These compounds contain tervalent arsenic and the preparation was undertaken with the hope that the presence of sulphur in the benzene nucleus might probably increase their trypanocidal value.

Our first attempt to prepare thiol-compounds was from potassium benzene sulphonate, which on being arsenated by Bechamp's method (*Compt. rend.*, 1863, **56**, 1172) was expected to react in the following manner:—

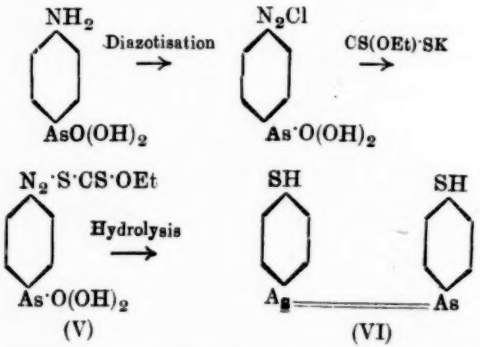


Compound (I) was formed but its purification was found to be a matter of considerable difficulty, the analytical results being far from satisfactory. (Found: As, 23·86 ; S, 11·8. $C_6H_7O_6SAs$ requires As, 26·6 ; S, 13·10 per cent.). The sulphonyl chloride (II) was found to be unstable and decomposed slowly into benzene sulphonyl chloride and arsenic acid which was deposited as a crystalline solid at the bottom of the container. When freshly prepared it contained 23·7 per cent. arsenic and on being left for 24 hours the arsenic content fell to 1 per cent. After attempting another unsuccessful scheme of preparation, namely,



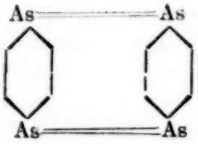
the following method was finally adopted:—

p-Arsanilic acid was diazotised and coupled with potassium ethyl xanthate in alkaline solution to give (V), which on hydrolysis yielded (VI).



The regulation of temperature at which the coupling took place was a matter of some importance. At low temperature, the coupling

did not proceed, while at the temperature of boiling water the xanthate decomposed. It was found that maximum coupling took place at 50—60°. The conversion of (V) into (VI) is probably in accordance with Lieb's experiments (*Ber.*, 1921, **54**, 1511) who converted *p*-phenylene diarsenic acid $AsO(OH)_2.C_6H_4{\cdot}AsO(OH)_2$ into



by heating the former at 50-60° for sometime.

The constitution of the thiolarsenobenzene, in all probability, is as shown in (VI) and this view has been further confirmed by preparing and studying some of its derivatives. It was found that cold hydriodic acid has no action on the compound but when heated with the acid and phosphorus it decomposed, one of the products being thiophenol. Similar results were obtained when thiolarsenide was heated for about eight hours with hydriodic acid under pressure at 120-130°. Oxidising agents, such as chlorine or dilute nitric acid, convert (VI) into the sulphonic acid, $SO_3H{\cdot}C_6H_4{\cdot}As{\cdot}O(OH)_2$, a substance soluble in water, and an insoluble diarsinic acid disulphide (IV) (Hewitt, King and Murch, *loc cit.*).

A number of additive compounds of 4 : 4′-dithiolarsenobenzene (VI) have been prepared and these, in all probability, possess the constitution of the type $R{\cdot}As{=}As{\cdot}R...A$ and $R{\cdot}As{=}As{\cdot}R...2A$, where A stands for the compound attached. These are in confirmation with the theory of residual affinity in case of one or both of arsenic atoms. It is well known that arsenobenzene and its derivatives form additive compounds of the type $R{\cdot}As{=}As{\cdot}R...MeX$ and $R{\cdot}As{=}As{\cdot}R...2MeX$, and the formation is presumably due to the residual affinity of one or both arsenic atoms, as arsenobenzene itself which contains neither the hydroxy- nor amino-groups can form such derivatives (Ehrlich, *Ber.*, 1915, **48**, 1634). It has been found that 4 : 4′-dithiolarsenobenzene (VI) combines with three molecules of acetyl chloride to give $[AcS{\cdot}C_6H_4{\cdot}As{=}As{\cdot}C_6H_4{\cdot}SAc]...CH_2{\cdot}COCl$ (VII), two molecules of acetyl chloride reacting with the thiol-group and a third molecule attaching itself to form an additive compound. With

thionyl chloride a slightly different type of compound namely (VIII) is formed.

$$\begin{array}{l} SOCl\cdot S\cdot C_6H_4\cdot As...SOCl \\ \quad\quad\quad\

Isolation of p-*Xanthyldiazobenzene Arsinic Acid* (V).

p-Arsanilic acid (2 g.) was dissolved in hydrochloric acid (3 c.c.) and diazotised in the usual manner with sodium nitrite (0·8 g.) dissolved in water (4 c.c.). The diazotised solution was next added to potassium ethylxanthate (1·5 g.) dissolved in potassium hydroxide (2 c.c. of 50 %) solution. A yellow crystalline powder (K-*salt*) separated which was quickly removed, washed with alcohol and ether and dried in a vacuum desiccator. (Found: As, 17·00. $C_9H_9O_4N_2S_2K_2As$ requires As, 17·60 per cent.).

Diacetyl-4 :4′-*dithiolarsenobenzene Acetyl Chloride* (VII).

To acetyl chloride (7 g.) the thiolarsenobenzene (2 g.) was added in small portions, when a vigorous action took place. The reaction was completed by heating the solution on a water-bath for half an hour and the cooled solution was poured into ice-cold water. A white solid separated which was crystallised from pyridine in colourless micro-prisms (yield, theoretical). It does not melt. (Found: As, 28·40 ; Cl, 6·58. $C_{18}H_{17}O_3ClS_2As_2$ requires As, 28·27; Cl, 6·6 per cent.).

4 :4′-*Dithiolarsenobenzene and Thionyl Chloride*: *Formation of* (IX).

4 :4′-Dithiolarsenobenzene (2 g.) was gradually added to thionyl chloride (5 c.c.). To complete the reaction the solution was heated on a water-bath for half an hour and then the cooled mixture was poured in cold water. A white solid separated out, which was filtered, dried and crystallised from alcoholic pyridine in small prismatic needles. The substance does not melt and becomes semi-solid and brown on standing in air. (Found: As, 25·80 ; Cl, 5·91. $C_{12}H_{11}O_6ClS_5As_2$ requires As, 25·14 ; Cl, 5·96 per cent.).

The *sodium* salt is easily prepared by dissolving the substance (1 g.) in sodium hydroxide solution (10 c.c. of 10 %). The residue obtained on drying the solution was crystallised from alcohol in colourless micro-crystalline powder. (Found: Na, 10·78. $C_{12}H_8O_6ClS_5Na_3As_2$ requires Na, 10·41 per cent.).

4 :4′-*Dithiolarsenobenzene Ethyl Chlorocarbonate*, $(SH{\cdot}C_6H_4{\cdot}As)_2{\cdot}\ldots Cl{\cdot}CO_2Et$.

The thiolarsenobenzene (2 g.) and ethyl chlorocarbonate (5 g.) were suspended in alcohol and saturated with dry hydrogen chloride. The

solution was filtered and poured into ice-cold water. A white solid separated which was filtered, dried and crystallised from alcohol in colourless micro-crystalline powder. The substance does not melt. (Found: As, 31·71; Cl, 6·88. $C_{15}H_{16}O_2ClS_2As_2$ requires As, 31·48; Cl, 7·45 per cent.).

4:4′-*Dithiolarsenobenzene Picrate*, $(SH{\cdot}C_6H_4{\cdot}As)_2.....2C_6H_2(NO_2)_3OH$.—Equal quantities of the thiolarsenobenzene and picric acid in alcohol were carefully heated on a water-bath for a short time and the mixture allowed to stand overnight. On treatment with acids a brown precipitate was obtained from the filtered solution from which the excess of picric acid was removed on boiling with alcohol, and the brown residue left behind was crystallised from pyridine in light brown micro-crystalline powder. It does not melt. (Found: As, 18·24. $C_{24}H_{16}O_{14}N_6S_2As$ requires As, 18·15 per cent.).

4:4′-*Dithiolarsenobenzene Perchlorate*, $(SH{\cdot}C_6H_4{\cdot}As)_2...2HClO_4$.

Perchloric acid (5 g.) was added to the thiolarsenobenzene (2 g.) in sodium hydroxide solution and the mixture heated on a water-bath for an hour. On cooling, the mixture was acidified, when a white crystalline mass separated, the purification of which was effected by repeated precipitation from its alkaline solutions by acid. It is a colourless micro-crystalline powder, insoluble in all the organic solvents and has no melting point. (Found: As, 26·25; Cl, 11·70. $C_{12}H_{12}O_8Cl_2S_2As_2$ requires As, 26·36; Cl, 12·47 per cent.).

4:4′-*Dithiolarsenobenzene Methiodide*, $(HS{\cdot}C_6H_4As)_2...2CH_3I$.

To an alkaline solution of the thiolarsenobenzene, methyl iodide was added at 40°. A vigorous reaction took place which was completed by warming on a water-bath. The solution on treatment with hydrochloric acid gave a yellow precipitate, which on drying was crystallised from alcohol in yellow micro-needles, which did not melt. (Found: As, 23·85; S, 9·29. $C_{14}H_{16}I_2S_2As_2$ requires As, 23·00; S, 9·81 per cent.).

4:4′-*Dithiomethylarsenobenzene Dimethylsulphate*, $(CH_3S{\cdot}C_6H_4{\cdot}As)_2...2(CH_3)_2SO_4$.

Dimethyl sulphate was slowly added to an alkaline solution of the thiolarsenobenzene. A vigorous reaction took place with evolution of heat. The solution was then heated on a water-bath, for about half an hour and on acidifying the cooled solution, a white precipitate

was thrown down which was collected, dried and crystallised from alcohol in colourless needles which do not melt. (Found: As, 22·7 . $C_{18}H_{26}O_8S_2As_2$ requires As, 23·14 per cent.).

4 :4′-*Dithiolarsenobenzene Hydrochloride*, $(SH{\cdot}C_6H_4{\cdot}As)_2....2HCl$.

The thiolarsenobenzene (2 g.) was suspended in concentrated hydrochloric acid and kept warm for several hours. It was then diluted with water and the white precipitate obtained was well washed. (Found: As, 34·73. $C_{12}H_{12}Cl_2S_2As_2$ requires As, 34·01 per cent.).

4 :4′-*Dithiolarsenobenzene Hydrogen Sulphate*, $(HS{\cdot}C_6H_4{\cdot}As)_2...2H_2SO_4$.

To a concentrated sulphuric acid (20 c.c.) the thiolarsenobenzene (2 g.) was gradually added with constant stirring. The mixture was then warmed to 50° for 2 hours, cooled and poured over ice. A white solid separated which was thoroughly washed with water and dried in a vacuum desiccator. It is a colourless crystalline powder having no melting point. (Found: As, 27·18. $C_{12}H_{14}O_8S_4As_2$ requires As, 26·59 per cent.).

Action of Oxidising Agents on 4 :4′-*Dithiolarsenobenzene.*

(a) *Chlorine.* 4 :4′-Dithiolarsenobenzene suspended in alcohol was saturated with dry chlorine gas when the suspended matter dissolved. The solution was then filtered, boiled with animal charcoal, evaporated to dryness and the residue was crystallised from absolute alcohol in colourless micro-crystalline powder, highly soluble in water. This substance is in all probability 1-sulpho-4-phenylarsinic acid, $SO_3H{\cdot}C_6H_4{\cdot}AsO(OH)_2$. (Found: S 11·43. $C_6H_7O_6SAs$ requires S, 11·34 per cent.).

(b) *Nitric acid.* 4 :4′-Dithiolarsenobenzene was heated with 30 per cent. nitric acid on a water-bath. On pouring the solution in water a light yellow precipitate was obtained, which was collected, washed and dried. The solid was found to consist of two substances one of which is soluble and the other completely insoluble in all the organic solvents.

The *insoluble* portion was purified by precipitating its alkaline solution with acids. Its reactions indicate that it is diphenyl disulphide 4 :4′-diarsinic acid. (Found: S, 14·00. $C_{12}H_{12}O_6S_2As_2$ requires

S, 13·73 per cent.). The disulphide is slightly soluble in dilute nitric acid from which it may be crystallised in needles.

The *soluble* portion was crystallised from alcohol in colourless micro-crystalline plates. It is probably a *p*-sulphophenyl arsinic acid, $SO_3H{\cdot}C_6H_4{\cdot}As{\cdot}O(OH)_2$. (Found: S, 11·28. $C_6H_7O_6SAs$ requires S, 11·34 per cent.). A further quantity of the sulpho-acid was obtained from the nitric acid mother-liquors on evaporation to a syrup with repeated addition of water to remove excess of acid. On careful evaporation in a desiccator, a crystalline mass was obtained, which was redissolved in water and crystallised by leaving a concentrated solution in a desiccator.

(c) *Hydrogen Peroxide.* 4:4′-Dithiolarsenobenzene was heated with hydrogen peroxide in an alkaline medium, on a water-bath for 4 hours. On making the solution acid a yellow precipitate was obtained which was collected and further purified by repeatedly dissolving in alkali and precipitating with acid. In this way a yellow micro-crystalline powder having the formula, $SH{\cdot}C_6H_4{\cdot}As{\cdot}O(OH)_2$ was formed. It does not melt but decomposes on heating above 250°. (Found: S, 13·41. $C_6H_7O_3SAs$ requires S, 13·67 per cent.).

Action of Hydriodic Acid.—4:4′-Dithiolarsenobenzene decomposes into thiophenol and arsenic acid when heated with hydriodic acid. A similar behaviour was observed when the substance was heated with hydriodic acid under pressure at 120–130°. Hydriodic acid was found to have no action at all on the substance in the cold.

Summary.

4:4′-Dithiolarsenobenzene has been prepared by coupling diazotised *p*-arsanilic acid with potassium ethylxanthate and hydrolysing the product. Analytical work shows it to have the formula, $SH{\cdot}C_6H_4{\cdot}As{=}As{\cdot}C_6H_4{\cdot}SH$ and this has been further confirmed by a study of its derivatives. 4:4′-Dithiolarsenobenzene has characteristic mercaptanic properties and forms additive compounds of the type $(SH{\cdot}C_6H_4{\cdot}As)_2{\ldots}A$ with acetyl chloride, thionyl chloride and ethyl chlorocarbonate. With hydrochloric acid, methyl iodide, dimethyl sulphate, picric acid, perchloric acid, etc., compounds of the type $(SH{\cdot}C_6H_4{\cdot}As)_2{\ldots}2A$ are formed. Reducing agents have practically no effect, while oxidising agents convert it into a disulphide $[AsO(OH)_2{\cdot}C_6H_4{\cdot}S]_2$ and a sulpho-acid $SO_3H{\cdot}C_6H_4{\cdot}AsO(OH)_2$.

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Studies in the Ligno-cellulose Group. Part. I. An Investigation into the Constituents of Water Hyacinth (*Eichornia Crassipes*).*

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The plant, according to a report of the Special Officer appointed by the Government of Bengal, spreads over an area of 4,269 square miles in ten of the badly infected districts of the province of Bengal, and is regarded as a menace to agriculture in general. The eradication of water hyacinth has thus become a problem of very great importance and attempts to destory it by spraying arsenic and other chemicals have been resorted to from time to time without any practical success. The high potassium chloride content already known, led the Department of Agriculture to establish an experimental station to extract this salt during the War-period. For various reasons, the chief amongst which being the adulteration of the ash with sand and earthly matters, the venture was discontinued and the programme of combating the growth of the weed in this way was abandoned. We were at this time examining the nature of cellulose in different species of wood with a view to their utilisation for the production of power alcohol. Our attention was naturally drawn to the plant, in view specially of its rich potash content, after extraction of which the fibre would be available for saccharification, and subsequent fermentation. Although the technical bearing of this problem would hardly be within the scope of this communication the chemical data accruing from this investigation are considered to be of sufficient interest and are recorded here.

The green plant, on drying in the sun, loses about 95% of its weight and shrinks into a pale yellowish brown straw with dark roots, having a volume approximately one fifteenth of the green substance. Analysis of the green plant shows it to contain 3·7% organic matter and 1·1% ash. Although the green plant in all its

* The samples examined in this paper were collected from the suburbs of Calcutta.

parts shows the presence of starch, the dry plant does not show a trace of it. If, however, the green plant is quickly dried in a steam-oven, the presence of starch is unmistakable. The probable inference, therefore, is that the disappearance of the starch on gradual drying is due to the photochemical decomposition of starch through the intervenion of chlorophyll. An analysis of the average root shows 0·07% starch which works out at approximately 1·4% on the air dried substance. The average content of starch in the leaf and the stem is 0·018% on the green substance or 0·36% on the air-dried. The recognition of the presence of starch is important in studying the bacterial fermentation of the green plant to which detailed reference will be made later.

In course of the experiment the root, the leaf and the stem as also the total weed have been separately investigated, both with regard to the potassium chloride content as also to the alcohol obtainable from them. As is obvious, to ascertain the relative proportion in weight between the different parts of water hyacinth is not very easy, as they differ greatly according to their growth. The average of several determinations may be given as below:

Stem	...	...	56·0 per cent.
Leaf	...	...	14·0
Root	...	...	30·0
		Total.	100·0

This, however, by no means, can be accepted as anything more than a very crude approximation. Experiments conducted to determine the percentages of ash and potassium chloride in the different parts of the dried plant gave the following results: –

	Stem.	Leaf.	Root.
Ash	... 24·9%	18·1%	23%
KCl	... 14·2%	5·5%	7·5%

The total plant on ignition leaves an ash, the percentage of which varies between 19·75 and 23 on the air dried substance. Below is a proximate analysis of the air-dried plant and its ash.

(a) *Analysis of the air-dried plant* :—

Moisture	13·46 per cent.
Soluble in benzene	1·15
* Soluble in benzene-alcohol mixture	7·70
Soluble in cold water	21·64
Soluble in hot water	23·64
Soluble in 1 per cent. NaOH	45·51
Lignin	11·31
Pentosan	13·33
Cellulose (Cross and Bevan's method).	21·89
Cellulose (ClO_2 method)	42·23
Total nitrogen (Kjeldahl)	1·45-1·73
Volatile matter	62·4
Total pentosan in cellulose (Cross & Baven) ...	1·53 gms
Total Pentosan in cellululose (ClO_2 method). ...	12·04
Total α-cellulose in cellulose (Cross & Bevan). ...	16·94
Total α-cellulose in cellulose (ClO_2 method). ...	16·49

The approximate percentage composition of the air-dried sample may therefore be represented as below :—

Moisture	13·46 per cent.
Ash	19·75
Fat & wax	7·70
α, β and γ-Cellulose ...	42·23
Lignin	11·31
Nitrogen and its compounds ...	5·55
Total =	100·00

Analysis of the Ash :—

	Sample I.	Sample II.
Cl'	24·18	25·56
CO''_3	4·92	6·46
SO_4''	4·68	4·72
P_2O_5	6·06	6·21
SiO_2	9·32	2·44
Fe_2O_3, Al_2O_3	13·21	13·31
CaO	9·08	9·39
Potassium	26·60	32·00
Sodium	2·02	

The high percentage of alumina led us to think that it might be due to any adhering clay. Sample I represents an ordinary sample but

* The extract contained practically no nitrogen. Nitrogen in the residue = 2·23%.

sample II represents a washed and cleaned sample. The difference, however, was only noticed in the silica-content which shows the general richness of the plant in alumina, as the iron is present only in traces in the ash.

The primary importance of the ash cannot be regarded as being wholly due to the large amount of potassium chloride present in it, as, in addition, quite a substantial amount of calcium phosphate and alkali carbonate are present in it (*vide* analysis). Extraction of the ash with water completely removes the chlorides, sulphates and a part of the carbonates giving a residue of calcium phosphate, calcium carbonate, alumina and silica. The percentage of alkali carbonate in the ash varies, according to the source of supply and the mode of incineration, from 1·5 to 9 per cent. If we accept any figure from 3 to 5% as average, the ash would then be comparable in richness to some of the alkali sands in India and Burma and as such, may be of some value. The insoluble calcium phosphate may be rendered available for use as manure, adding thereby to the value of the dried plant.

Acetylation of the dried Water hyacinth.

This was attempted in order to obtain some fresh information as to the condition in which lignin is present in a ligno-cellulose, that is to say, whether it exists in chemical combination or in physical adsorption. 10 Gms. of the dried water hyacinth were ground and passed through a seventy mesh sieve ; this was extracted in a Soxhlet apparatus for 18 hours with a mixture of equal volumes of benzene and absolute alcohol, in order to free it from fat and resin and then heated with 60 gms. of acetic anhydride to boiling under reflux for 15 hours on a sand-bath. The mass was filtered, washed repeatedly with acetic anhydride and finally with chloroform in order to remove any soluble triacetate (of which there was practically very little). The mass was next extracted with boiling ether in a Soxhelt apparatus in order to remove the least trace of acetic acid and acetic anhydride that might have been left. This was then finally dried in vaccum before analysis. A weighed quantity of the product was treated with a definite volume of $N/10$-coustic soda and allowed to stand 24 hours after which period the excess of alkali was titrated with $N/10$-sulphuric acid. The amount of alkali which was used up was expressed in term of CH_3CO. Thus, in a typical example, 0·6314 gm. of the acetylated product

required 38·0 c.c. of $N/10$-alkali for saponification, corresponding to 25·89% CH_3CO. A blank on the powder before acetylation correspended to 5·6% CH_3CO. The acetylation was thus effected upto 21·74%.[1] The acetylated product, however, contained the lignin and ash which can be seen from the following analysis: –

Lignin	...	...	...	12·44 per cent.
Residue after ClO_2 treatment			...	67·40
Ash	...	...	...	17·28
Pentosan	...	...	...	14·80

The cellulose acetate was separated from the lignin by treatment of the acetylated product with a 2% solution of chlorine peroxide free from hydrochloric acid and chlorine. The acetyl value of the acetate left was 30·27% corresponding to 20·4% CH_3CO on the initial acetylated product. This would seem to indicate that the acetylation, on treatment with acetic anhydride, was restricted mostly to the cellulose part of the ligno-cellulose, the blank acetyl value probably referring in part, at any rate, to lignin and hemi-cellulose. It should also be noted here that in the process of acetylation, the hemi-cellulose part is not removed as the product contained 14·8% pentosan and gave on saccharification with concentrated hydrochloric acid 42·6% reducing sugar. If, on the other hand, the raw material is first deprived of its lignin content by treatment with chlorine peroxide and the total cellulose so obtained acetylated as before, then the acetylated product contains 23·48% CH_3CO and making correction for the blank which was found to contain 3·6% CH_3CO, it becomes only 20·82% CH_3CO and not 30·27%. This difference may be due either to a change in the general constitution of cellulose by the treatment of chlorine peroxide or by the delignification of the original fibre. If the delignification causes a change in the chemical constitution of cellulose, it may not be far wrong to conclude that lignin was probably in chemical combination with the cellulose. On treatment of the acetylation product of the cellulose prepared by the chlorine peroxide method, with 17·5% caustic soda solution in the cold for 30 minutes, 59·3% of its weight is lost, indicating the removal not only of the acetyl group but also of the

[1] 100 grams of the acetylated fibre contain $100-25·89=74·11$ grams fibre. Blank on the fibre $=5·6\%$ CH_3CO or $74·11\times5·6\times\frac{1}{100}=4·15$ on 74·11 grams of fibre. Therefore % of fibre acetylated $=25·89-4·15=21·74$.

hemi-cellulose portion. This latter is obtained on acidification of the alkali extract with acetic acid as a white amorphous powder. It is worthy of notice here that on acetylation of fibre by boiling with acetic anhydride, a cellulose acetate goes into solution which can be precipitated by ether and can be crystallised from chloroform. This corresponds to a triacetate and has the same acetyl value and physical characterestics as those of the one obtained by acetylating either the crude or the chlorine peroxide-cellulose by a mixture of acetic acid and acetic anhydride in presence of concentrated sulphuric acid to the extent of 5% of the weight of the acetylating mixture. The acetyl value of such an acetate was found to be 44·97% (triacetate requires 44·79% CH_3CO). The quantity, however, of the triacetate obtained in the filtrate by the anhydride process is very small. The residue from the acetylation of the chlorine peroxide-cellulose by the cold method, contained 15·8% CH_3CO. The action of chlorine peroxide on the acetylated product, whether from the crude or from the purified cellulose, does not cause any alteration in the acetyl value, although lignin or acetylated lignin is removed by it. It was also found that the acetyl value of the triacetate remained unchanged after treatment with chlorine peroxide. That the hemi-cellulose remains intact after acetylation is proved by the fact that the pentose-content practically suffers no diminution. Thus 0·6714 gm. acetylated crude fibre on distillation with hydrochloric acid (*d* 1·06) and precipitation of the distillate with phloroglucinol, gave 0·1072 gm. phloroglucide corresponding to 14·8% pentosan (calculated pentosan = 14·53%). Further, as mentioned above, treatment of acetylated chlorine peroxide-cellulose with 17·5% caustic soda for 30 minutes, removes the hemi-cellulose and the acetyl groups, leaving α-cellulose behind: 0·8576 gm. acetylated chlorine peroxide-cellulose on treatment with 17·5% caustic soda solution in the cold for half an hour and then on being washed with 8% caustic soda, dilute acetic acid and finally with distilled water till free from acetic acid, gave on drying 0·3496 gm. α-cellulose corresponding to 40·7% α-cellulose. This is equivalent to 22·2% α-cellulose on the dried crude fibre. The α-cellulose on the dried crude fibre was found to be 21·3%. The behavior of the triacetate, that is, the variety which is soluble in chloroform and acetone, is however different. The action of 17·5% alkali removes only the acetyl group leaving the pure α-cellulose behind. It should be noticed in this connection that the chlorine peroxide-cellulose shows

in the blank an acid value of 3·6%. It is reasonable to expect that in the absence of lignin which was dissolved out by the chlorine peroxide solution, this acid value is anchored on to the hemi-cellulose part.

Lignin isolated by Willstätter's method on acetylation with acetic anhydride by boiling for 15 hours on a sand-bath, required caustic soda corresponding to 23·74% CH_3CO. The blank corresponded to 12·56% CH_3CO.[2]

Saccharification of Water hyacinth.

As the conversion of the cellulosic material into fermentable sugars formed the chief objective of this work, it was conducted under widely different conditions with a view to determine the most suitable one for the technical production of "power alcohol." The air-dried plant was accordingly treated with sulphuric or hydrochloric acids of various strengths at different temperatures (autoclaves being used where necessary). The plant was either treated with the acid after extraction of soluble matter by boiling with water (or 5% solution of sulphuric acid) or the plant was directly treated with the acid after extraction of soluble matters by water digestion under pressure and heat. The general methods followed in the experiments were as follows:—

(1). *Saccharification after extraction with boiling water.*—10 Gm. of air-dried plant cut into small pieces were repeatedly boiled with water till the filtrate showed the absence of chlorides. The remaining fibre on being dried at 105° weighed about 6·3 gm. The total filtrate was evaporated to dryness and carefully ignited at

[2] Of the three methods generally adopted for acetylation, we have intentionally followed the anhydride boiling process in this work in order to avoid as far as possible any change taking place in the cellulose or ligno-cellulose complex. Acetylation in the presence of a catalyst, for instance, sulphuric acid, introduces the possibility of some sort of hydrolytic change, and as such cannot be regarded as being free from objections. While in a subsequent communication we hope to throw some more light on the nature of combination between the cellulose and the lignin complex, it may be stated at this stage that the isolation of a triacetate soluble in chloroform takes place only after some change in the cellulose is brought about by the catalyst, and as such, the formation of a diacetate by anhydride boiling whether of the purified cellulose or of the crude ligno-cellulose fibre, can be held as a sort of evidence in favour of the chemical combination of cellulose with lignin in ligno-cellulose. This statement, however, is made with great reservation at this stage.

a low heat in order to avoid volatilisation of potassium chloride. On being titrated with $N/10$-silver nitrate, the following percentages of chlorides calculated as KCl were obtained:—

Expt. No. ...	38	47	50	53	54	55	56	306
KCl (per cent.)	12·00	11·80	10·88	12·22	12·75	10·90	9·68	12·97

Mean 11·65%.

The residue (63%) still contained about 0·20 to 0·21 per cent. chloride in it and a content of ash varying from 5 to 7% on the weight of the original plant.[3] The main filtrate on evaporation to dryness leaves a soft solid which was found to contain 0·408% nitrogen on the original air dried plant corresponding to 2·57% of proteid matter. The residual fibre still contained 0·924% nitrogen. It was also noticed that the residue contained 20·6% pentosan, *i.e.*, 12·98 on the original fibre and hence the extraction of the plant with boiling water practically removed no pentosan.

The residual fibre was next treated with varying quantities of sulphuric acid at various dilutions under different pressures in the autoclave. A few of the results are given in the Table I below.

TABLE I.

Saccharification of air-dried water hyacinth after extraction with boiling water.

Vol. of dil acid to 100 gm. original.	Wt. of H_2SO_4 to 100 gm. original.	Pressure in atmospheres.	Time in minutes.	Per cent. of Reducing sugar on original.	Per cent. of pentose on original.
700 c.c.	2 gm.	6	30	5·0	—
,,	4	,,	,,	9·7	—
,,	8	,,	,,	11·6	9·6
,,	4	9	,,	9·8	—
200	,,	,,	,,	8·7	—
700	8	,,	,,	12·8	9·8
,,	18	3	60	15·2	—
,,	18	,,	30	13·2	—

[3] *N.B.*—Henceforth all the results will be expressed and the calculations made on the air-dried water hyacinth unless otherwise stated.

It is interesting to note here that in cases where the yield of sugar was very low, the solution on hydrolysis by heating with dilute hydrochloric acid at 80° gave a reducing value corresponding to about 8 to 9% reducing sugar. Estimation of pentose by distilling the solution with 12% hydrochloric acid solution gave from 9 to 10% pentose calculated on the original fibre. The sugar solution was practically unfermentable, only 7 to 10% at the most suffered fermentation by yeast. Osazone prepared from this solution melted at 159-160° and hence it was concluded that the sugar was practically pentose. Hydrolysis of the residue for the second time with varying concentration of acid under different pressures was further studied which, however, gave a very small yield of sugar (3-6%) of which about 50% was fermentable. It was thought advisable, therefore, to deprive the plant of its pentose-yielding constituents and then effect the hydrolysis. Accordingly, experiments were conducted to determine the suitability of pentosan extraction by boiling with an excess of 5% sulphuric acid on the assumption that such a treatment might perhaps convert the cellulosic material into such a condition that further hydrolysis with dilute acids under pressure might give a greater yield of fermentable sugar with minimum quantity of acid.

(2) *Saccharification after extraction of the hyacinth with 5% sulphuric acid by boiling.*—100 Gm. air-dried water hyacinth cut into small pieces were boiled with 1500 c.c. of 5% sulphuric acid solution for half an hour. The remaining fibre, on being washed, pressed and dried, weighed on an average 40-42 gm. An estimation of sugar in the filtrate gave about 12-13% reducing sugar and contained on an average 9·4-10·2% chloride calculated as potassium chloride. Most part of the sugar was pentose but occasionally 3 to 4 per cent. hexoses were also present. In this operation 2-5 gm. of sulphuric acid were used up, but the solution could be used over and over again for the extraction of a few fresh lots of water hyacinth. It was found that sulphuric acid of strengths 2-4% required a good length of time to free the plant of its pentosan content. But the volume of the 5% acid solution could be profitably diminished to 500 c.c. if the boiling be continned for at least 4-5 hours with a reflux condenser. Subsequent saccharification was done on the residue thus obtained and a few results calculated on the original air-dried plant are given in Table II.

TABLE II.

Saccharification of the residue after boiling air-dried water hyacinth with 5% sulphuric acid.

Vol. of acid on 100 gm. of the original.	Wt. of acid on 100 gm. of the original.	Pressure in atmospheres.	Time in minutes.	Sugar on original.
400 c.c.	2 gm.	10	30	3·96 per cent.
200	6	,,	,	2·72
400	,,	,,	,,	3·42
,,	8	8	,,	2·19
,,	,,	9	45	3·44
,,	,,	,,	30	3·72

From the above table it is evident that the yield of reducing sugar can hardly be expected to be greater than 4%. As the amount of pentoses present in the sugar solution as determined by the phloroglucinol method rarely exceeded 1·2%, it was believed that most of the sugar was fermentable. This was further corroborated by fermentation experiments which showed that on an average 75-85% of the sugar was fermentable. A second hydrolysis of the residue with 8% sulphuric acid and 200 c.c. of water at 9 atomspheres for 15 minutes gave the best yield of reducing sugar *i.e.*, 3·0%, of which about 95% was fermentable.

(8) *Direct saccharification of the air-dried water hyacinth by dilute sulphuric acid.*—In the process of boiling water hyacinth with 5% sulphuric acid as a preparatory treatment for the production of a residue most suitable for the hydrolysis to follow, most of the potassium chloride and the pentose-yielding constituents present in the raw fibre were no doubt removed, and even admitting that the potassium chloride could be recovered, the process required a large excess of sulphuric acid and the yield of sugar was not good. Hence our investigation was carried out directly on the air-dried water hyacinth without any previous treatment. The hyacinth was digested directly with dilute acids under pressure, expecting that this may extract the potassium chloride, the pentosans and perhaps some appreciable quantities of fermentable sugar in addition. A few of the results are given in the following table.

TABLE III.

Saccharification of 100 gm. air-dried water hyacinth with dilute sulphuric acid.

1st Hydrolysis.						2nd Hydrolysis.					
Vol. of dil. acid (c.c.).	Wt. of acid. (gm.).	Press. in atms.	Time in mints.	Sugar %.	Pentose %.	Vol. of dil. acid (c.c.).	Wt. of acid. (gm.)	Press. in atmos.	Time in mints.	Sugar %	Fermentation %.
200	0·25	6	15	2·83	...	200	8	8	30	7·15	...
,,	,,	8	,,	3·70	...	300	6	9	,,	6·35	...
,,	1·0	10	,,	4·40	...	400	8	10	,,	5·14	...
,,	2·0	,,	,,	7·35	...	...	...	...	...	...	...
,,	,,	,,	30	8·10	...	...	...	...	...	...	...
100	,,	9	15	7·50	...	400	8	9	30	6·50	...
200	3·0	3	,,	4·90	...	80	,,	,,	,,	11·54	55
,,	,,	,,	60	11·70	...	,,	,,	,,	,,	9·48	69
,,	4·0	,,	15	5·10	...	60	6	10	,,	8·45	59
700	,,	9	30	8·30	...	...	...	...	...	...	...
200	6·0	8	15	7·00	...	...	...	...	...	...	...
330	8·0	9	,,	10·30	...	330	8	9	15	5·00	...
700	9·0	3	60	14·00	12·57	...	...	...	...	...	...
,,	18·0	,,	,,	15·00	10·09	...	...	...	...	...	...
,,	,,	,,	30	13·75	12·13	700	8	9	30	4·35	...

Though the amount of sugar obtained in the first hydrolysis varied between wide limits under varying conditions of pressure and quantity of acid used, it is to be noted here that the sugar solution on further hydrolysis gave a reducing value corresponding on an average to 8·5% reducing sugar and hence the results are similar to those of the hydrolysis of the residue after extraction with boiling water. All the potassium chloride was practically removed. Only a little fermentable sugar was obtained as was evident from the fact that the hydrolysed solution contained about 10-12% of pentoses. A second hydrolysis gave sugar of which on an average 50-60% was fermentable but no regularity was observed in their yields. The conjecture, therefore, was that the cellulose on heating with dilute acids under pressure becomes somewhat modified in its properties, depending upon the condition to which it is subjected. Since acids as weak as 0·25% can extract the pentosan, it was expected that perhaps a

simple hot water digestion under high pressure may serve the purpose and leave the cellulosic material unmodified as far as the saccharification process is concerned.

(4) *Saccharification of water hyacinth after water digestion under pressure.*—After a large number of experiments, it was found that 100 gm. of air-dried water hyacinth heated with 200 c.c. of water at 9 atmospheres for 15 minutes effected the extraction of potassium chloride as well as 85-90% of the pentosans present in the raw material. The liquid extract was made up to a known volume and an aliquot part carefully evaporated and incinerated gave the following percentages of chlorides calculated as potassium chloride.

Expt.	... 37	43	45	49	53	91	701	109	
KCl.	... 8·55	14·35	9·25	10·3	10·0	12·39	13·58	12·32	14·
Expt.	... 307	312	372	116	121	124	140	141	
KCl.	... 12·72	11·92	12·99	16	13·36	10·77	14·35	13·48	

Mean. 12·15%

The analysis of a sample of potassium chloride derived from the plant is given below:—

Qualitative:—Na, K, Mg. (trace), SO''_4, Cl′, CO''_3, $Fe(CN)'''_6$ (trace) CNS′ (trace), NO'_2 (trace).

Quantitative:—

Cl′	45·10 per cent.
SO''_4	2·70
CO''_3	0·60
Potassium	49·90
Sodium	1·60
Mg, $Fe(CN)_6$,''' CNS, etc. ...	0·10
Total	100·00

The potassium chloride so obtained is therefore 95·3% pure and is of a high grade of purity. If instead of using 2 parts of water for every one part of the raw material, less quantity of water were used, the mass became charred thereby causing damage to the cellulosic material.

The residue from the pressure-water digestion was subjected to hydrolysis as usual under different conditions. A few of the typical results are given in Table IV.

TABLE IV.

Saccharification of 160 *gm. air-dried water hyacinth after pressure water-digestion.*

1st hydrolysis.						2nd hydrolysis.					
Vol. of dil. acid (c.c.).	Wt. of acid (gm.).	Press in atoms.	Time in mins.	Sugar %	Fermentation %.	Vol. of dil. acid (c.c.).	Wt. of acid (gm.)	Press in atmos.	Time in mins.	Sugar %	Fermentation %.
250	1·0	9	30	3·17	...	250	1·0	9	30	0·57	...
,,	2·0	,,	,,	4·08	...	,,	2·0	,,	,,	3·80	...
500	2·5	,,	,,	5·49	...	,,	2·5	,,	,,	2·75	...
210	,,	,,	,,	8·20	...	120	5·0	,,	,,	4·50	...
500	3·0	,,	,,	6·90	...	500	3·0	,,	,,	2·81	...
250	4·0	6	,,	8·3	62	,,	4·0	6	,,	1·80	...
200	4·5	9	15	8·5	40	100	2·25	9	15	4·5	...
,,	5·0	,,	,,	8·2	...	,,	,,	,,	,,	3·4	...
210	,,	,,	,,	8·97	42	210	5·0	,,	,,	4·3	80
230	,,	,,	,,	8·85	46	100	2·5	,,	,,	1·81	...
,,	,,	,,	,,	,,	,,	120	,,	,,	,,	1·90	...
,,	,,	,,	,,	,,	,,	,,	50	,,	,,	3·10	...
240	,,	,,	,,	8·21	...	100	2·5	,,	,,	3·40	...
250	,,	,,	,,	6·40	...	...	...	...	...	...	...
500	,,	,,	,,	6·40	...	...	...	...	...	...	...
1000	,,	,,	4·5	7·8	53·3	250	8·0	8	30	3·07	...
,,	,,	,,	,,	,,	,,	500	5·0	,,	45	2·60	...
,,	,,	,,	,,	,,	,,	1000	,,	,,	,,	2·53	...

TABLE IV (*continued*).

1st hydrolysis.						2nd hydrolysis.					
Vol. of dil. acid (c.c.)	Wt. of acid (gm.)	Press. in atmos.	Time in mins.	Sugar %	Fermentation %.	Vol. of dil. acid (c.c.)	Wt. of acid (gm.).	Press. in atmos.	Time in mins.	Sugar %	Fermentation %.
30	6·0	9	30	4·42	...	60	·0	9	30	7·13	85
80	,,	,,	,,	5·90	...	...	...	...	...	...	...
160	,,	,,	,,	7·70	...	...	...	...	...	...	...
200	,,	,,	15	7·34	...	300	6·0 ,,	8	30	3·9	...
,,	,,	,,	,,	,,	...	60	,, ,,	9	,,	7·13	85
250	,,	,,	,,	9·64	...	250	,, ,,	,,	15	5·30	83
80	8·0	9	,,	7·50	72						
160	,,	,,	,,	8·40	80						
200	,,	,,	30	7·80	...						
,,	,,	,,	5	2·96	...						
300	,,	,,	30	7·60	35	400	8·8	8	30	·17	...
330	,,	,,	15	9·60	67	330	,,	,,	15	4·93	78
,,	,,	,,	,,	,,	,,	120	3·0	,,	,,	2·90	81
400	,,	,,	30	8·50	45	400	2·0	9	30	1·30	...
,,	9·0	,,	,,	8·70							
250	10·0	8	5	2·65	...						
1000	,,	,,	30	8·75	...						
700	18·0	3	60	16·00	18	4	2·0	9	30	3·9	...

From an analysis of the tables above, it would appear that a semi-normal solution of sulphuric acid under a pressure of 9 atmospheres causes the best saccharification, and that in the second acid hydrolysis, the reducing sugar is practically completely fermentable, indicating the presence of small quantities of pentose only. From a consideration of the technical feasibility of the process it has been found that a fairly good yield of fermentable sugar is obtained by using on the air-dried water hyacinth 4·5% sulphuric acid for the first hydrolysis and 2·25% sulphuric acid for the second.

The residue left after the pressure-water digestion of 100 gm. air-dried water hyacinth is about 62 gm. and contains 0·789 gm. nitrogen, 0·901 gm. of nitrogen having passed into the extract. The residue after the first hydrolysis with 4·5% acid at 9 atmospheres weighs about 42 gm. and on further hydrolysis with 2·25 gm. acid at 9 atmospheres, weighs about 25 gm. and has a calorific value of 7700 B.Th.U. Its appearance is brownish black and is quite suitable as fuel, specially under a somewhat forced draught. The final residue still retains 0·32% nitrogen.

(5) *Saccharification with concentrated hydrochloric acid.* Experiments were also conducted to study the amount of reducing sugar obtainable by saturation of the hyacinth by hydrochloric acid gas at different temperatures. The material was taken in a round bottom flasked moistened with three times its weight of water and hydrochloric acid gas passed through the mass, which was kept at a definite temperature by providing cooling arrangements till no further absorption took place. The flask was tightly corked and allowed to stand for an hour at the room temperature, at the end of which the acid was removed by a suction pump. When the major portion of hydrochloric acid was removed which was evident from the disappearance of frothing, the temperature was gradually raised to 70° on a water-bath. The suction was continued till the mass became nearly dry when sufficient quantity of water was added so that the acidity of the solution was reduced to about 1%. This required water about 10 times the weight of the hyacinth taken. This was boiled for an hour, filtered and washed. The filtrate was neutralised with chalk and again filtered. The sugar content of the solution was estimated and then it was subjected to fermentation. The amount of fermentable sugar was estimated by direct titration as also from a determination of the specific gravity of the distillate obtained by the fractional distillation of

the fermented liquor. The mean of several experiments are given in the Ttable V. It will be found that the maximum yield of sugar on an average is 34·12%. In some of the experiments reducing value as high as 39·2% was obtained corresponding to 95% of the theoretical yield on cellulose and hemi-cellulose combined. During the course of the experiments, preliminary trials were made to study the significance of the process of boiling after the hydrochloric acid had been removed by suction. It was found that before boiling, about 40% of the totally available sugar was already present in the filtrate. It is thus probable that an ester of hydrochloric acid is first formed with the cellulose which gradually breaks down into simple reducing sugars even at ordinary temperatures but more so, at higher temperatures. Further experiments in this direction are in progress. The table also shows that the concentration of hydrochloric acid plays an important part in the process of saccharification and that fermentation by yeast is not inhibited by the presence of chlorides in the solution to an extent hitherto believed.

TABLE V.

Saccharification by concentrated hydrochloric acid.

(*a*) 100 gms. air-dried water hyacinth was taken.

Expt.	Temp.	Sugar.	Fermentation.
394	0°	34·12 per cent.	60 per cent.
186	10°	31·80	51
285	20°	26·64	44
279	30°	24·06	38

(*b*) Residue from 100 gms. air-dried water hyacinth after pressure-water digestion.

...	0°	26·30	80
...	10°	22·68	75
...	20°	19·80	71
...	30°	15·70	66

(*c*) Residue from 100 gms. air-dried water hyacinth left after successive digestien with water and 5% sulphuric acid at 9 atoms.

127	0°	12·6	90·0

(*d*) Residue from 100 gms. air-dried water hyacinth left after successive digestion under 9 atmospheric pressures with water, 5% sulphuric acid and 2·5% sulphuric acid.

Expt.	Temp.	Sugar.	Fermentation.
197	0°	7·47	95·0

Saccharification of cellulose.—Saccharification of different kinds of celluloses prepared from water hyacinth was also studied with 5% sulphuric acid and 10 times water at 9 atmospheres for 15 minutes. The following results were obtained:—

Nature of cellulose.	Sugar.	Contribution of sugar from 100 gms. hyacinth.
Cellulose (Cross and Bevan) ...	19·53 per cent.	4·07
α-Cellulose from Do ..	19·16	3·26
Cellulose (chlorine peroxide) ...	25·80	10·84
α-Cellulose from Do ...	20·70	3·41

It is evident from the above table that the α-cellulose becomes modified, if at all, to the same extent by the chlorine or chlorine peroxide treatment. The cellulose prepared by ClO_2 method was also digested with water at 9 atmospheres for 15 minutes; on estimation of sugar in the filtrate, it was found to yield 5·22% sugar. The sugar solution on hydrolysis corresponded to an yield of 11·72% reducing sugars. The presence of hemi-cellulose in chlorine peroxide cellulose is thus proved.

Bacterial decomposition of the plant.

The large quantity of hemi-cellulose present in the plant suggested the possibility of easier disintegration of the hyacinth fibre by the action of bacteria. We understand similar work is being carried out by Dr. G. J. Fowler in the Sir Harcourt Butler Technological Institute, Cawnpore. As our preliminary results appear sufficiently encouraging, a short summary of the work is given below. In all our experiments we used septic tank fluids and the green plant in preference to the dried one as the latter did not decompose as readily as the former. The fermentation which commenced within a day or two after the addition of the tank-liquor continued over several days till a p_H value of 3·8 was reached. At this stage the concentration of potassium chloride was 0·2% and that of acid 0·0727% in term of acetic acid. The temperature employed was 38°-40°. A typical experiment

yielded 1800 c.c. of gas in course of seven days from 100 gm. green water hyacinth having the following compositions:—

	I	II	III	IV
CO_2 ...	22·1	21·6	21·4	21·3
O_2 ..	1·2	1·4	1·6	1·5
CH_4 ...	51·6	52·7	52·8	52·7
H_2 ...	25·4	25·0	24·6	21·5

The residual pulp from the above experiment was treated with chlorine peroxide solution, in order to estimate the quantity of α, β- and γ-celluloses remaining after fermentation.

100 Gm. green water hyacinth contained 2·1500 gms. total cellulose.

After fermentation and chlorine peroxide treatment, total cellulose is equal to 1·3760 gm. (containing 0·8430 gm., α-cellulose. Therefore the total cellulose fermented is equal to 0·7740 gm. of which 0·533 gm. was hemi-cellulose and 0·241 gm. α-cellulose. This corresponds to a fermentation of 36% of the total cellulose. The volume of gas is however not commensurate with these figures even after allowing for a control experiment and the probable contribution of starch. Further experiments with thermophylic bacteria are in progress.

Destructive distillation of the air-dried plant.

Distillation of 10 gm. of air-dried water hyacinth at 1000° gave about 4·8 litres of gas and a residue of 18% charcoal. The distillation at 500° left 40% charcoal. The composition of the gas is given below:—

	At 1000°.	At 500°
Carbon dioxide	8·31	36·90
Unsaturated hydrocarbon ...	Trace.	3·75
Marsh gas	11·53	10·94
Carbon monoxide	25·74	14·06
Hydrogen	33·30	24·5
Oxygen	2·57	3·12
Nitrogen	18·56	6·75

It would be interesting to conduct experiments to see how far the Mond-gasification of this plant may have any technical importance.[1]

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[1] Dr. R. L. Datt, Industrial Chemist to the Government of Bengal, first drew our attention to Mond-gasification of the plant.

Reviews

Kurzer Leitfader Der Photo-chemie by PROF. Dr. J. PLOTNIKOW. The author has earned a great reputation as an investigator in the domain of Photochemistry. His Lehrbuch Der Photo-chemie and Photo-chemische Versachstechnic are standard books on the subject. A short introductory text book on photochemistry from the pen of Prof. Plotnikow should, therefore, be welcome to a large circle of readers. The book contains a large amount of information presented in a very simple and readable style. Some of the experiments described are suitable for class demonstration. The book will also prove very useful to the members of the medical profession who specialise in light-therapy. Prof. Plotnikow has indeed removed a long felt want by writing an elementary text book on Photochemistry.

J. C. G.

Experimentelle Einführung in die Unorganische Chemie by HEINRICH BILTZ. The book is the 15th to the 17th edition of the well known book by Heinrich Biltz. It is an elementary treatise on analytical chemistry. After dealing with the simple laboratory operations of filtration, evaporation, glass manipulations, cork-boring etc., it gives the individual tests and reactions of the common acids and bases. The usefulness of the book has been increased by the introduction of several chapters, dealing with theoretical considerations, which are necessary for the understanding of analytical process. The binding and printing of the book are quite up to the mark.

S. R. D. G.

Qualitative Analyse by HEINRICH BILTZ. This eleventh and the twelvth edition of the book may be looked upon as the second part of the book—"Experimentalle Einführung in die Unorganische Chemie" —as it deals with the methods for the analysis and identification of unknown substances. First of all, a general treatment on the preliminary operations necessary for the identification of substances is given. The metals and the acids are classified into different groups in accordance to their characteristic common reactions, and their individual tests as well as their methods of separation are given. An English rendering of the books may well serve as a good laboratory companion to B.Sc. students of our Universities.

S. R. D. G.

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ERRATA

Page	Line					
324	6*	Table VII (column 2nd)	*For*	0·4	*Read*	0·04
350	34		,,	Kiasiakowsky	,,	Kistiakowsky.
432	14 and 15		,,	Sb_2S_3	,,	$Sn(OH)_4$.
435		Table VI (column 3rd)	,,	3 hos	,,	3 hrs.
453	8*	(column 6th)	,,	50	,,	5·0.
454	9*	(column 6th)	,,	1·24	,,	12·4.
457	6*	(column 3rd)	,,	0·925	,,	0·0925.
457	16*	(column 6th)	,,	·68	,,	68.

* From bottom.

Photochemical Reaction between *cyclo*Hexane and Chlorine in Carbon Tetrachloride Solutions.

By Kali Pada Basu.

Photochemical reactions involving chlorine have always been a fascinating though somewhat puzzling problem to the photo-chemists. To elucidate the action of light on chlorine, the author has already studied the mechanism of an additive reaction involving chlorine in solution *viz.*, the photochemical reaction between cinnamic acid and chlorine (*J. Indian Chem. Soc.*, 1929, **6**, 341). In this communication the results of the study of a substitution reaction involving chlorine—the photochemical action of chlorine on *cyclo*hexane—will be described. The previous paper should be referred to for information about the purification of solvent, preparation of chlorine and other details.

The chlorination of *cyclo*hexane has not been studied by any previous investigator. The photo-bromination of *cyclo*hexane vapour has been studied by Pusch (*Z. Elektrochem.*, 1918, **24**, 336), Noddack (*ibid*, 1921, **27**, 359) and recently by Wood and Rideal (*J. Chem. Soc.*, 1927, **131**, 2466). Pusch and Noddack found the quantum efficiency of the reaction to be unity, and wood and Rideal find that the reaction gives unimolecular constants unaffected by changes in temperature or concentration of the acceptor and directly proportional to the intensity of radiation.

Kahlbaum's *cyclo*hexane was shaken with concentrated sulphuric acid and distilled. The reaction vessel ($4 \times 4 \times 1$ cm.) with plane parallel glass sides was placed inside a double jacketted metal box maintained within $\pm 0{\cdot}1°$ by circulation of water. The reaction-cell had a narrow opening at the top provided with a closely fitting stopper. The reaction was followed by pipetting out 2 c. c. from time to time, and the chlorine determined iodometrically with $N/200$-sodium thiosulphate which was prepared afresh, and standardised before each experiment.

The Dark Reaction.

In perfectly dry carbon tetrachloride solutions, the reaction between *cyclo*hexane and chlorine in the dark was, as Table I will show, negligible at 27°.

TABLE I.

The Dark Reaction.

*cyclo*Hexane = M/3. Chlorine = M/69. Temp. = 27°.

Time in mins.	*N*/200-Thiosulphate.	Unimol. const. log $a/(a-x)$.
0	11·60 c. c.	—
45	11·55	0·0000422
141	11·45	0·0000404
231	11·35	0·0000411
321	11·30	0·0000347
441	11·20	0·0000347
		Mean 0·0000386

On raising the temperature to 32° the mean unimolecular constant for the dark reaction was found to be 0·000044.

The reaction proceeded fairly quickly under stimulus of radiation from a quartz mercury lamp run from a storage battery under a constant current of three amperes. The kinetics of the reaction was studied in white light, the reaction cell being at a distance of 25 cm. and a water-filter, 4 cm. thick being placed between. As the following tables will show the reaction with an excess of *cyclo*hexane gave a unimolecular constant with respect to chlorine, the constant showing a tendency to fall off towards the end of the reaction.

With excess of *cyclo*hexane the reaction proceeded till the chlorine completely disappeared. As it was not possible to estimate the *cyclo*hexane along with chlorine one cannot definitely say how many molecules of chlorine ultimately reacted with a molecule of *cyclo*hexane when excess of the latter was employed. With an initial concentration of chlorine about double that of *cyclo*hexane, it was found that the completion of the reaction corresponded to about three atoms of chlorine reacting with one molecule of *cyclo*hexane.

In this investigation an excess of *cyclo*hexane was always employed. Under such conditions the reaction rate was found to be unimolecular with respect to chlorine showing that the reaction mainly consisted in the formation of the monochloro-substitution product. The value of the unimolecular constant showed a tendency to diminish as the reaction progressed. This point will be discussed later on.

Tables II-V indicate the typical results, while Table VI summarises the results at different concentrations of *cyclo*hexane and chlorine. The temperature was 27·8° throughout. The unimolecular constants are all on the basis of logarithm to the base 10 and time is reckoned in minutes.

TABLE II.

*cyclo*Hexane = *M*/3. Chlorine = M/60.

Time (mins.)...	0	10	25	40	65	85
N/200-$Na_2S_2O_3$...	12·85	11·25	9·4	7·9	6·1	5·0 c.c.
Unimol. const. ...	—	0·00578	0·00543	0·00529	0·00498	0·00482

Mean—0·00510.

TABLE III.

*cyclo*Hexane = M/3. Chlorine = M/46.

Time (mins.) ...	0	10	25	45	70	115
N/200-$Na_2S_2O_3$...	17·4	15·25	12·75	10·25	8·15	5·55 c.c.
Unimol. const. ...	—	0·00573	0·00540	0·00511	0·00470	0·00431

Mean—0·00505

TABLE IV.

*cyclo*Hexane = M/30. Chlorine = M/60.

Time (mins.) ...	0	10	25	40	60	92
N/200-$Na_2S_2O_3$...	13·35	11·95	10·35	8·9	7·45	5·65 c.c.
Unimol. const....	—	0·00481	0·00442	0·00440	0·00422	0·00406

Mean—0·00438

TABLE V.

*cyclo*Hexane = M/1·5. Chlorine = M/65.

Time (mins.) ...	0	10	25	45	67	90
N/200-$Na_2S_2O_3$...	12·1	10·0	7·85	6·0	4·55	3·6 c.c.
Unimol. const. ...	—	0·00828	0·00752	0·00677	0·00634	0·00585

Mean—0·00695

TABLE VI.

Conc. of *cyclo*hexane.	Conc. of chlorine.	Mean unimol. const.
M/1·5	*M*/65	0·00695
M/3	*M*/60	0·00510
M/7·5	*M*/60	0·00468
M/36	*M*/60	0·00438
M/37·5	*M*/60	0·00388
M/8	*M*/108	0·00443
M/3	*M*/76	0·00490
M/3	*M*/63	0·00510
M/3	*M*/46	0·00505

It will be seen from above that similar to the observations of Wood and Rideal on the bromination of *cyclo*hexane vapour (*loc. cit.*), the unimolecular constant is practically independent of the initial concentration of chlorine. The unimolecular constant, however, continually increases as the concentration of the acceptor (*cyclo*-hexane) increases.

Wood and Rideal maintain that in the bromination of *cyclo*hexane the unimolecular constant is independent of the initial concentration of the acceptor. A consideration of their values reproduced in Table VI (A) at once shows that the unimolecular constant distinctly increases slowly with increase in concentration of the acceptor if we only omit the value for *cyclo*hexane vapour pressure of 3·93 cm.

TABLE VI (A).

*cyclo*Hexane vapour pressure.	Bromine vapour pressure.	$K \times 10^4$.	*cyclo*Hexane vapour pressure.	Bromine vapour pressure.	$K \times 10^4$.
7·13 cm.	2·10 cm.	198	3·93 cm.	1·79 cm.	187
6·10	2·01	186	3·12	1·53	178
5·24	2·25	182	2·11	1·96	161

Effect of Hydrochloric Acid.—It will be observed that the unimolecular constant with respect to chlorine has a tendency to diminish as the reaction proceeds. It was thought that the hydrochloric acid generated in the reaction might have a retarding action. Experiments were, therefore, carried out in the presence of hydrochloric acid. Hydrochloric acid generated by the action of pure concentrated sulphuric acid on pure concentrated hydrochloric acid was washed successively through water, sulphuric acid and carbon tetrachloride and then dissolved in carbon tetrachloride. Tables VII and VIII will indicate that hydrochloric acid has no retarding effect but a very slight accelerating effect.

TABLE VII.

*cyclo*Hexane = M/3. Chlorine = M/60. HCl = M/55·5. Temp. = 20°.

Time in mins. ...	0	11	25	40	60	80
N/200-Thiosulphate...	13·25	11·45	9·55	7·85	6·10	4·95 c.c.
Unimol. const. ...	—	0·00576	0·00569	0·00568	0·00562	0·00535

Mean—0·00562

TABLE VIII.

*cyclo*Hexane = M/3. Chlorine = M/60. HCl = M/18·5. Temp. = 28°.

Time in mins.	...	0	10	25	40	60	87
N/200-Thiosulphate	...	13·0	11·3	9·25	7·55	6·0	4·5 c.c.
Unimol. const.	...	—	0·00608	0·00591	0·00590	0·00560	0·00530

Mean—0·00576

In the absence of hydrochloric acid, the mean value of the unimolecular constant is, from Table II, 0·00510. In the presence of the acid also, the unimolecular constant appears to diminish as the reaction progresses. The effect is, therefore, to be ascribed to the disturbing influence of the other reaction product, *viz.*, the chloro*cyclo*hexane.

Experiments in Monochromatic Light.

The quantum efficiency, temperature coefficient and the influence of intensity of radiation were then determined at wave-lengths 36 ·5$\mu\mu$, 404$\mu\mu$ and 436$\mu\mu$. The same filters were employed to isolate the different lines as was done in the chlorination of cinnamic acid (*loc. cit.*) with the difference that for the wave-length 436$\mu\mu$ the 2 cm. water filter was replaced by a 2 cm. filter of copper sulphate solution (20 gm. in 100 c.c.).

The intensity measurements were carried out with a Moll thermopile and a Moll galvanometer calibrated with a Hefner lamp at a distance of 100 cm.

The following experiments (Tables IX—XI) were carried out at 27°; a lower temperature could not be employed as further lowering of the temperature resulted in the deposition of moisture on the reaction vessel.

TABLE IX.

Intensity of incident radiation = 1·3 Hefners—at—100 cm.

Wave-length = 436$\mu\mu$. *cyclo*Hexane = M/3. Chlorine = M/65. Temp. = 27°.

Time in mins.	...	0	15	35	60	86	110
N/200-Thiosulphate	...	12·4	11·6	10·7	9·5	8·7	8·0 c.c.
Unimol. const.	...	—	0·00193	0·00183	0·00193	0·00179	0·00173

Mean—0·00184

Subtracting the dark reaction, the true light reaction is 0·00180.

TABLE X.

Intensity of incident radiation = 0·18 Hefners—at—100 cm.

Wave-length = 404$\mu\mu$. *cyclo*Hexane = M/3. Chlorine = M/66.
Temp. = 27°.

Time in mins.	...	0	15	45	90	150	206	
N/200-Thiosulphate	...	12·1	11·8	11·3	10·8	10·0	9·5	c.c.
Unimol. const.	...	—	0·000727	0·000660	0·000549	0·000552	0·000510	

Mean—0·000600

The light reaction constant is thus 0·000561.

TABLE XI.

Intensity of incident radiation = 0·11 Hefners—at—100 cm.

Wave-length = 366$\mu\mu$. *cyclo*Hexane = M/3. Chlorine = M/60.
Temp. = 27°.

Time in mins.	...	0	20	46	80	125	185	
N/200-Thiosulphate	...	13·05	12·7	12·3	11·9	11·25	10·50	c.c.
Unimol. const.	...	—	0·000585	0·000557	0·000500	0·000515	0·000509	

Mean—0·000533

The light reaction constant is 0·000494.

Quantum Efficiency at Various Wave-lengths.—The light absorbed was measured by taking galvanometer readings with the reaction cell filled with the solvent, and with chlorine solution of requisite strength. 1 Mm. of galvanometer deflection corresponded to 9 ergs per sq. cm. per sec.

At 436$\mu\mu$. The light absorbed corresponded to 18 mm. of galvanometer deflection. No. of quanta absorbed per sq. cm. per sec. therefore

$$= 18 \times 9 \times \frac{436 \times 10^{-7}}{3 \times 10^{10}} \times \frac{1}{6{\cdot}5 \times 10^{-27}}$$

$$= 3{\cdot}6 \times 10^{13} \text{ quanta per sq. cm. per sec.}$$

The change in chlorine concentration (Table IX) equals 0·8 c.c. of N/200 in 2 c.c. in 15 mins.

No. of mols. changed per sq. cm. per sec.

$$= \frac{{\cdot}80}{2} \times \frac{1}{2 \times 2} \times \frac{1}{100} \times \frac{1}{1000} \times \frac{1}{15 \times 60} \times 6{\cdot}1 \times 10^{23}$$

$$= 6{\cdot}78 \times 10^{14}.$$

$\therefore$ The quantum efficiency = 19 mols. per quantum.

At 404$\mu\mu$. The radiation absorbed was equivalent to 4 mm. No. of quanta absorbed per sq. cm. per sec. = $7{\cdot}43 \times 10^{12}$. Table X shows that the change in chlorine concentration was 0·8 c.c. of $N/200$ in 2 c.c. in 45 mins.

No. of molecules reacted per sq. cm. per sec. = $22{\cdot}59 \times 10^{13}$.

Hence about 30 molecules reacted per quantum of light absorbed.

At 366$\mu\mu$. Absorption corresponded to 3 mm. of galvanometer deflection. No. of quanta absorbed per sq. cm. per sec. = $5{\cdot}067 \times 10^{12}$. Chlorine transformed (Table XI) = 0·75 c.c. of $N/200$ in 2 c.c. in 46 mins. No. of mols. transformed per sq. cm. per sec. = $20{\cdot}7 \times 10^{13}$. Thus about 41 molecules reacted per quantum of radiation absorbed.

The quantum efficiency of this reaction is thus very large. This must be ascribed to a reaction chain set up as a result of absorption of radiation. Quantum efficiency also increases as the frequency of the incident radiation increases.

Temperature Coefficient at different Wave-lengths.

The experiments in monochromatic lights of the same intensity and with the same initial concentrations were then performed at an elevated temperature (32°). The corresponding velocity constant for the dark reaction is, as already mentioned, 0·00004.

Table XII summarises the results at 32° after deducting the dark reaction.

TABLE XII.

Wave-length.	*cyclo*Hexane conc.	Chlorine conc.	Mean unimol. const.
436 $\mu\mu$	$M/3$	$M/65$	0·00221
404 $\mu\mu$	$M/3$	$M/69$	0·000637
366 $\mu\mu$	$M/3$	$M/66$	0·000557

Table XIII gives the temperature coefficients of the reaction at different wave-lengths.

TABLE XIII.

Wave-length ...	436$\mu\mu$	404$\mu\mu$	366$\mu\mu$
Temp. coefficient ...	$\left(\frac{0{\cdot}00221}{0{\cdot}00180}\right)^2$	$\left(\frac{0{\cdot}00637}{0{\cdot}00561}\right)^2$	$\left(\frac{0{\cdot}000657}{0{\cdot}000494}\right)^2$
	$=1{\cdot}50$	$=1{\cdot}29$	$=1{\cdot}26$

for 10° interval,

The temperature coefficient thus increases in wave-length and is in accordance with the well-known ideas of Tolman (*J. Amer. Chem. Soc.*, 1923, **45**, 2285).

Influence of Intensity on Reaction Rate.—A knowledge of the influence of intensity of incident radiation on the reaction rate is essential in order to arrive at any satisfactory mechanism of the reaction. Experiments were, therefore, performed at a lower intensity of light of wave-length 436$\mu\mu$ at temperatures 27° and 32°. The intensity was varied by altering the distance of the lamp from the reaction cell. The higher intensity (Tables IX and XII) corresponded to a galvanometer deflection of 131 mm., the lower intensity to a deflection of 67 mm. The ratio of the incident intensities was thus 2·0.

Table XIV gives the reaction at lower intensity of 436 $\mu\mu$.

TABLE XIV.

Intensity of 436$\mu\mu$=0·67 Hefners-at-100 cm.

*cyclo*Hexane=M/3. Chlorine=M/65. Temp.=27°.

Time in mins.	N/200-Thiosulphate.	Unimol const.
0	12·3 c.c.	—
15	11·95	0·000833
35	11·56	0·000834
70	10·86	0·000807
115	10·0	0·000782
160	9·25	0·000774
	Mean	0·000806

The light reaction is thus 0·000768.

At a temperature of 32° and *cyclo*hexane concentration of $M/3$ and chlorine $M/6$, the light reaction constant at the same intensity as Table XIV above 0·000907.

The ratio of the velocity constant at the two intensities

$$\left(\frac{0{\cdot}00221}{0{\cdot}000907} = 2{\cdot}4, \text{ and } \frac{0{\cdot}00180}{0{\cdot}000768} = 2{\cdot}36 \right) \text{ is, therefore, } 2{\cdot}4.$$

The reaction is thus directly proportional to the intensity of incident radiation. The same relation was obtained by Wood and Rideal in the bromination of *cyclo*hexane vapour (*loc. cit.*).

After-effect.—Since the reaction had a very large quantum efficiency it was expected that it would show quite an appreciable after-effect. Experiments, however, failed to detect any marked after-effect.

The Mechanism of the Reaction.—The main features of the reaction are the following:—(1) The photochemical reaction between *cyclo*hexane and chlorine appears to be unimolecular with respect to chlorine. The value of the constant is directly proportional to the intensity of incident radiation. It is independent of the concentration of the chlorine and increases slightly as the concentration of the acceptor increases. The constant gradually falls off as the reaction progresses, and hydrochloric acid is without any influence. The quantum efficiency of the reaction is very large and increases with increase in frequency of the incident radiation. The reaction shows no induction period or appreciable after-effect.

A mechanism of reaction has got to be found which explains all the observed facts.

The primary action is the action of the absorbed quantum on the chlorine molecule. In the bromination of *cyclo*hexane vapour where the quantum efficiency is unity and there is, therefore, no reaction chain and the reaction rate is found to be directly proportional to the intensity, Wood and Rideal favour the formation of excited bromine molecules rather than that of atoms.

The formation of excited chlorine molecules can scarcely explain the large quantum efficiency observed in this reaction. Moreover, the numerous experiments of Ghosh and his collaborators in this laboratory, of Bödenstein, Berthoud and the work of Franck leave no room for doubt that the primary action of a light quantum ($\lambda < 4785$ Å) on a halogen molecule is dissociation of the molecule into a normal and an excited atom. In the previous paper on the chlorination of cinnamic acid, this point has been considered in some detail.

It seems at first inconsistent with the hypothesis of formation of atoms that the reaction rate in a chain reaction should be directly proportional to the intensity of incident radiation rather than to its square-root. In what follows a chain reaction is indicated which explains all the observed facts.

The primary action of the light quantum ($\lambda < 4785$ Å) is

$$Cl_2 + h\nu \longrightarrow Cl + Cl \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

As already indicated in the chlorination of cinnamic acid the life of excited chlorine formed on absorption of light is very great and the

reverse reaction ($Cl + Cl \longrightarrow Cl_2$) is, therefore, very slow and can be neglected compared with the other possible reactions.

The following chain reaction thus takes place :—

$$C_6H_{12} + Cl = C_6H_{11}Cl + H \quad \ldots \quad \ldots \quad (2)$$
$$H + Cl_2 = HCl + Cl \quad \ldots \quad \ldots \quad (3)$$
$$H + C_6H_{11}Cl = C_6H_{12} + Cl \quad \ldots \quad \ldots \quad (4)$$
$$H + Cl = HCl \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

Reaction (4) explains the inhibiting action of the monochloro-substitution product. Indicating the respective velocity constants of the above reactions by k_1, k_2, k_3, k_4 and k_5, we shall deduce an expression for the rate of formation of $C_6H_{11}Cl$.

Since the absorption was small, the light absorbed equals $I_0[Cl_2]$ where I_0 is the intensity of incident radiation.

$$\frac{+d[Cl]}{dt} = k_1 I_0 [Cl_2] + k_3[H][Cl_2] + k_4[H][C_6H_{11}Cl]$$

$$\frac{-d[Cl]}{dt} = k_2[C_6H_{12}][Cl] + k_5[H][Cl]$$

In the steady state these are equal.

Again $$\frac{+d[H]}{dt} = k_2[C_6H_{12}][Cl]$$

$$\frac{-d[H]}{dt} = k_3[H][Cl_2] + k_4[H][C_6H_{11}Cl] + k_5[H][Cl]$$

In the steady state they are equal. We have then

$$2k_1 I_0[Cl_2] + k_3[H][Cl_2] + k_4[H][C_6H_{11}Cl] = k_2[C_6H_{12}][Cl] + k_5[H][Cl] \quad \ldots \quad (A)$$

$$k_3[H][Cl_2] + k_4[H][C_6H_{11}Cl] + k_5[H][Cl] = k_2[C_6H_{12}][Cl] \ldots (B)$$

Subtracting (B) from (A) we have

$$[Cl] = \frac{k_1 I_0[Cl_2]}{k_5[H]} \quad \ldots (C)$$

From (B) we have

$$[H] = \frac{k_2[C_6H_{12}][Cl]}{k_3[Cl_2]+k_4[C_6H_{11}Cl]+k_5[Cl]} \quad \ldots \text{(D)}$$

Now

$$\frac{d[C_6H_{11}Cl]}{dt} = k_2[C_6H_{12}][Cl]-k_4[H][C_6H_{11}Cl]$$

$$= k_2[C_6H_{12}][Cl]\left\{1-\frac{k_4[C_6H_{11}Cl]}{k_3[Cl_2]+k_4[C_6H_{11}Cl]+k_5[Cl]}\right\}$$

$$= k_2[C_6H_{12}][Cl]\left\{\frac{k_3[Cl_2]+k_5[Cl]}{k_3[Cl_2]+k_4[C_6H_{11}Cl]+k_5[Cl]}\right\}$$

$$= \frac{k_1k_2[C_6H_{12}]I_0[Cl_2]}{k_5} \cdot \frac{k_3[Cl_2]+k_5[Cl]}{k_2[C_6H_{12}][Cl]}$$ substituting for [Cl] and from (B).

$$= \frac{k_1I_0[Cl_2]}{k_5[Cl]} \times k_3[Cl_2]+k_1I_0[Cl_2]$$

$$= k_3[H][Cl_2]+k_1I_0[Cl_2].$$

Since [H] is very small, $\frac{d[C_6H_{11}Cl]}{dt}$ or the rate of reaction will be mainly given by $k_1I_0[Cl_2]$. In other words the reaction should be unimolecular with respect to chlorine and the unimolecular constant should be directly proportional to the intensity of incident radiation. This has been realised in the experiments.

The slight accelerating effect of increase in concentration of the acceptor and the retarding action of the monochloro-substitution product becomes clear if we take into consideration the term $k_3[H]$

$[Cl_2]$. From (C) and (D) we have the following quadratic equation in $[H]$.

$$[H]^2\{k_5k_3[Cl_2]+k_5k_4[C_6H_{11}Cl]\}+k_1k_5I_0[Cl_2][H]$$
$$-k_1k_2[C_6H_{12}]\ I_0\ [Cl_2]=0$$

or

$$[H]=\frac{-k_1k_5I_0\ [Cl_2]\ \sqrt{\{k_1k_5I_0[Cl_2]\}^2+4k_1k_2[C_6H_{12}]I_0[Cl_2]\{k_5k_3[Cl_2]+k_5k_4[C_6H_{11}Cl]\}}}{2\{k_5k_3[Cl_2]+k_5k_4[C_6H_{11}Cl]\}}$$

It is clear from above that $[H]$ increases with increase in the concentration of the acceptor and diminishes as the concentration of chloro*cyclo*hexane increases. Here is thus an explanation for the observed effect of the concentration of the acceptor and of the reaction product on the velocity of reaction. A complete theoretical explanation has thus been furnished for the experimentally observed facts.

The increase in quantum efficiency with increase in frequency can be explained in the same way as in the chlorination of cinnamic acid. With increase in frequency of the absorbed quantum ($\lambda <$ 4785 A°) the kinetic energy of the atoms formed increases and this energy is communicated to the reaction products. The greater the frequency, the greater will be the energy o fthe products and consequently the longer the chain.

Photo-chlorination in Solutions.—This work as well as the previous one on the chlorination of cinnamic acid makes it abundantly clear that almost the same difficulties surround chlorination reactions in solution as in the gaseous state. The life of the excited chlorine appears to be very great in solution as well. The quantum efficiency, though not as great as in the combination of hydrogen and chlorine, is still considerably greater than unity showing complicated chain reactions. It is indeed remarkable that no induction period or after-effect could be detected in either of these reactions. In solution one disturbing and complicating factor is absent and that is oxygen.

Summary.

The photochemical reaction between *cyclo*hexane and chlorine in carbon tetrachloride solutions has been studied in white as well as in monochromatic light. The reaction gives a unimolecular constant with respect to chlorine, that is independent of the concentration of chlorine and increases slowly with increase in concentration of the acceptor. The reaction constant is directly proportional to the intensity of incident radiation. The constant slightly falls off as the reaction progresses and hydrochloric acid is without any influence. The quantum efficiency is 19 at 436$\mu\mu$, 30 at 404$\mu\mu$ and 41 at 366$\mu\mu$. The temperature coefficient is 1·5 at 436$\mu\mu$, 1·29 at 404$\mu\mu$ and 1·26 at 366$\mu\mu$. An explanation of the observed facts is given and an expression for the reaction rate derived on the basis of the following mechanism : –

$$Cl_2 + h\nu \longrightarrow Cl + Cl \quad \ldots (1)$$

$$C_6H_{12} + Cl \longrightarrow C_6H_{11}Cl + H \quad \ldots (2)$$

$$H + Cl_2 \longrightarrow HCl + Cl \quad \ldots (3)$$

$$H + C_6H_{11}Cl \longrightarrow C_6H_{12} + Cl \quad \ldots (4)$$

$$H + Cl \longrightarrow HCl \quad \ldots (5)$$

My best thanks are due to my professor, Dr. J. C. Ghosh for his kind interest and many valuable suggestions.

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The Effects of Electrodeless Discharge on Potassium Chlorate, Bromate and Iodate.

By Sampuran Das Mahant.

In a previous paper Bhatnagar, Sharma, and Mitra (*J. Indian Chem. Soc.*, 1928, **5**, 379) have shown that under the influence of electrodeless discharge naphthalene is converted into a compound whose composition is represented by the empirical formula $C_{24}H_{20}O$. J. J. Thomson (*Proc. Phys. Soc., Lond.*, 1928, **40**, 79) has further shown that the gas through which the electrodeless discharge passes enters into chemical combination and produces compounds some of which are quite unexpected. The discharge evidently puts some of the atoms and molecules into an excited state which enhances their chemical activity. Thus he found that magnesium oxide under the influence of the discharge combines with oxygen to form a higher oxide. Similar results were obtained with calcium oxide and zinc oxide.

The present communication deals with the effects of the eletrodeless discharge on potassium chlorate, bromate and iodate. These substances have been found by the author to emit a beautiful blue fluorescence in a Tesla tube. Incidentally the behaviour of molecules when excited by such agents as heat and ultra-violet light has been compared with what happens under the Tesla discharge.

Experimental.

The apparatus for obtaining the electrodeless discharge was the same as described by Bhatnagar, Shrivastava, Mathur, and Sharma (*Phil. Mag.*, 1928, p. 1227) with the modification that the X-ray dental transformer was replaced by a Siemens transformer having a ratio of 200 primary to 45,000 secondary.

The substance to be exposed was put in the discharge tube and a glass plate was cemented on to one end of the tube by Everette's vacuum wax. The other end of the tube was drawn out and connected to a manometer through a wash-bottle containing liquid paraffin. The manometer was connected to a Cenco Hyvac pump *via* another wash-bottle which also contained liquid paraffin. All

joints were made air-tight with Everette's wax and the tube was exhausted to a pressure of 1—3 mm. of mercury when the discharge was allowed to pass for 7 hours generally. The glow obtained varied in colour in the case of chlorate from violet to sky blue, light to dark violet and sometimes sky blue in the case of bromate and bright violet in the case of iodate. The substance in the tube was shaken from time to time to expose a fresh surface to the discharge. After exposure the substance was taken out of the discharge tube by removing the glass plate. All the work was carried out at the room temperature.

Tests and Estimations.

Chlorate.—When taken out of the tube, the exposed sample of the chlorate exhibited a blue opalescence which disappeared in the course of 24—48 hours. The sample also smelt distinctly of chlorine and gave tests showing the presence of chloride and hypochlorite. A sample of the original chlorate was tested for these radicles but gave negative results. No chlorite and perchlorate could be detected in the exposed sample. The following types of results were obtained with 100 gm. of exposed potassium chlorate.

	Expt. 1.	Expt. 2.	Expt. 3.
Hypochlorite ...	0·001636 g.	0·001680 g.	0·005303 g.
Chloride ...	0·1509	0·1600	0·16525

Bromate.—When taken out of the discharge tube the bromate gave a smell of bromine and showed tests corresponding to the production of a hypobromite and bromide. No free bromine could be detected. The original sample of bromate did not give any tests for hypobromite and bromide. The following results were obtained with 100 g. of exposed potassium bromate.

	Expt. 1.	Expt. 2.	Expt. 3.
Hypobromite ...	0·001388 g.	0·001491 g.	0·002111 g.
Bromide ...	0·08364	0·09770	0·05097

Iodate.—The iodate when removed from the tube had acquired a brownish colour and smelt and gave tests showing the presence of free iodine. No iodide could be detected. 100 Gm. of exposed iodate gave 0·02199, 0·02205, and 0·01610 g. of iodine in three different experiments.

Owing to the low pressure at which the work was carried out, the gases evolved during the course of the decomposition could not be removed from the system. Attempts were made to identify the gases by placing aqueous solutions of suitable reagents in the system but it was found that as soon as any aqueous solution was introduced, sufficiently low pressures could not be obtained and the glow was inhibited. In one of these attempts it was noticed that when the pressure in the system was 13—15 mm. and the discharge has been allowed to pass for a sufficient length of time, the exposed iodate was white in colour, had no brownish speck and did not smell of iodine. Analysis of the sample showed that hypoiodite had been formed, the original not containing this.

Several devices were tried to test if any oxygen was evolved during the decomposition. Although traces of oxygen were detected by the usual alkaline pyrogallol test, the quantities evolved were so small that no quantitative measurements were possible.

The results, though of considerable theoretical and practical interest, are incapable of quantitative repetition on account of the difficulties in manipulating the experiments. The different factors which affect the results are :—

(1) Voltage at which the discharge passes.
(2) The length of exposure.
(3) The amount of substance exposed.
(4) The surface exposed to the discharge, it being evidently a surface phenomenon.
(5) The number of times the surface is renewed by shaking.
(6) The intervals at which the shaking is effected.
(7) The pressure in the system.

Conclusion.

The decomposition of potassium chlorate, bromate and iodate under the Tesla discharge may be expressed as follows :—

$n\mathrm{KClO_3}$ decomposes into $(n-1)\mathrm{KCl} + \mathrm{KClO} + [(3n-1)\mathrm{O}]$
$n\mathrm{KBrO_3}$,, ,, $(n-1)\mathrm{KBr} + \mathrm{KBrO} + [(3n-1)\mathrm{O}]$
$n\mathrm{KIO_3}$,, ,, $n\mathrm{I} + [3n\mathrm{O}]$.

Bhatnagar, Sharma, and Mitra (*loc. cit.*) and J. J. Thomson (*loc. cit.*) have shown that under the influence of electrodeless discharge, oxidation occurs. The results now obtained show that

with certain substances reduction can also take place. The products obtained are not those which are obtained when these substances are heated or when they are exposed to the ultra-violet radiations as the following table shows:—

Exciting agent.	Potassium chlorate.	Potassium bromate.	Potassium iodate.
Heat.	KCl + Oxygen *via* $KClO_4$ with traces of Cl.[1]	KBr + Oxygen with traces of bromine.[2]	KI + Oxygen with traces of iodine, no per- or other oxy-salts at any stage of decomposition.[3]
Ultra-violet radiation.	Oxygen + KCl[4]	Oxygen + KBr[4]	Oxygen + KI + I[4]
Electrodeless discharge.	KCl + KClO	KBr + KBrO	Iodine.

From the above it will be clear that no hypo-salts have been detected as a result of the decomposition of the chlorate, bromate and iodate either by heat or ultra-violet radiations. In the case of chlorates, the perchlorate is formed but the per-salts have not been detected in the case of the iodates.

In these experiments the presence of per-salts has not been detected. Hypochlorite and hypobromite have been detected. Ordinarily these salts are not produced by decomposition of the chlorate and bromate; in fact they are oxidised to the chlorate and bromate. In the case of iodates, iodine has been found to be present and the presence of iodides has not been detected. The invidious results in the case of iodates may be explained by assuming that $KIO_3 \rightarrow KI + KIO$ and that KI and KIO further react to form I and K_2O. The reaction $KI + KIO + H_2O \rightarrow I + KOH$ has been studied by Schonbein (*J. pr. Chem.*, 1861, *i*, **84**, 385), and Taylor (*Chem. News*, 1897, **76**, 27; *J. Chem. Soc.*, 1900, **77**, 725), who have shown it to be a reversible one. Evidence of the presence of potassium hypoiodite was found in the decompostion of potassium iodate at a pressure of

[1] Rilliet and Crafts (*Brit. Assoc. Rep.*, 1882, p. 493); Teeds (*J. Chem. Soc.*, 1887, **51**, 283); Frankland and Dunglwall (*ibid*, p. 274); Schonbein (*J. pr. Chem.*, 1855, *i*, **65**, 96); Leeds (*Chem. News*, 1880, **42**, 304); Cook (*J. Chem. Soc.*, 1894, **65**, 802).

[2] Stas (*Mem. Acad. Belgique*, 1865, **35**, 116); Cook (*loc. cit.*).

[3] Rammelsburg (*Pogg. Ann.*, 1869, **137**, 307; 1839, **44**, 577); Cook (*loc. cit.*).

[4] Oertel (*Biochem. Z.*, 1914, **60**, 480; *J. Chem. Soc.*, 1914, **106**, 321); Suryanarayana (*J. Sci. Assoc. of Maharaja's College, Vizianagram*, 1924, **2**, 12; *Chem. Abs.*, 1924, **18**, 3548); Mathews and Curtis (*J. Phys. Chem.*, 1914, **18**, 641).

13—15 mm. Attempts were made to test the complete validity of this view by testing the residue left after extraction of the free iodine with carbon disulphide but it was found that it gave a neutral reaction to litmus.

The results outlined above show that the effect of the electrodeless discharge on potassium chlorate, bromate, and iodate is not analogous to the effect of heat or ultra-violet radiations.

A theoretical explanation of these results will be given in a subsequent paper.

This work was suggested by Prof. S. S. Bhatnagar, D.Sc. (Lond.), F.Inst.P., and the best thanks of the author are due to him for his useful suggestions and valuable guidance during the course of this investigation.

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Reduction of Mercuric Chloride by Glycerol.

By M. N. Goswami and P. N. Ganguly.

In the course of a preparative work we had to use mercuric chloride and glycerol; our attention was directed to the remarkable ease with which the former became reduced. Blank tests were performed with the exclusion of other organic compounds and it was found that it was glycerol which was responsible for the reduction.

Studies were then instituted to find out the conditions under which the reduction of mercuric chloride was maximum and to ascertain the nature of the products. It was found that the liquid, after the removal of mercurous and mercuric chlorides, contained glyceric aldehyde, and moreover there was copious evolution of a gas which was found to contain formaldehyde and acrolein. The formation of glyreric aldehyde is not a novel feature in the reaction. As early as 1895 Diacon (*Bull. Soc. Chim.*, 1895, *iii*, **13**, 862) observed its formation from mercuric chloride and glycerol but so far, no further work appears to have been done on the subject with a view to examine the gaseous products or to study the condition of formation of mercurous chloride.

It appeared from an examination of the reaction products that mercuric chloride acted in three different ways: (*i*) It first oxidised glycerol to glyceric aldehyde. (*ii*) It also dehydrated glycerol to acrolein. (*iii*) The glyceric aldehyde was then spilt up into formaldehyde probably *via* glycollic aldehyde:

$$CH_2OH{\cdot}CHOH{\cdot}CHO = CH_2O + CH_2OH{\cdot}CHO = 3CH_2O.$$

Glycerol has been oxidised to glyceric aldehyde by many workers using different reagents, *e.g.*, platinum black (Grimaux, *Compt. rend.*, 1887, **104**, 1276); nitric acid (Fischer and Tafel, *Ber.*, 1887, **20**, 1088); bromine (Fischer and Tafel, *Ber.*, 1888, **21**, 2634); ferrous sulphate and hydrogen peroxide (Fenton and Jackson, *J. Chem. Soc.*, 1899, **75**, 4) and oxygen in the presence of sunlight (Fenton and Jackson, *J. Chem. Soc.*, 1899, **75**, 10). Using lead peroxide Glaser and Morawski (*Monatsh.*, 1890, **10**, 578) obtained about 97% yield of formic acid whilst glyceric acid was obtained by Börnstein by the use of mercuric oxide and baryta (*Ber.*, 1886, **86**, 3357). The most interesting

results from the point of view of the present work were obtained by Bierry, Henry, and Ranc (*Compt. rend.*, 1911, **152**, 535; 1912, **154**, 1261) who used ultra-violet rays and got formaldehyde along with glyceric aldehyde from glycerol.

Since glycerol has been directly obtained from suger in good yield (D.R.-P. 347604) and starch easily yields glucose, a tentative chart of degradations linking starch and formaldehyde may be prepared:

Starch→glucose→glycerol→formaldehyde.

Different conditions under which mercuric chloride is required, have been carefully studied and it has been found that at 180-182° the reduction is maximum and amounts to 88—90%. The following chart illustrates the results obtained.

Percentage of Conversion.

Glycerol. (c.c.)	Water (c.c.)	$HgCl_2$ (gm.).	Temp.	Duration of heating.	Hg_2Cl_2 % conversion.
1·2	15	9·6408	30°	3 hrs.	Nil.
1·2	15	9·0525	60—70°	,,	0·12
1·2	15	9·31	100°	,,	0·15
1·5	80	12·0711	180°	,,	0·60
1·6	80	12·972	100°	,, (under pressure)	0·80
1·6	60	10·003	120—25°	,, ,,	0·36
5·5	nil	5·6262	100—05°	3 hrs.	0·33
10·5	nil	6·836	120—25°	,,	1·80
10·5	nil	5·0045	150—55°	,,	46·71
5·5	nil	5·550	180—82°	,,	88·00 (A)
5·5 (anhydrous)	nil	5·1568	150—55°	,,	52·90
5·5 ,,	nil	5·8708	180—82°	,,	90·20
6·0 ,,	nil	6·348	150—55°	,,	50·20
6·0 ,,	nil	5·0549	180—82°	,,	89·10

The gases obtained from experiment (A) were absorbed in water and the aqueous solution was analysed.

The simultaneous formation of the two volatile aldehydes in the reaction produced difficulties in their identification and estimation.

The former was done after fixing the unsaturated aldehyde by hydrochloric acid as β-chloropropionic aldehyde, neutralising the mass with sodium carbonate and distilling off the formaldehyde; it responded to all its essential tests including the very delicate test of Remini (formation of a brilliant magenta colour with phenylhydrazine hydrocloride, patassium ferrocyanide and hydrochloric acid). The estimation of formaldehyde was done by Romijn's method (*Z. anal. Chem.*, 1897, **36**, 18) while the total aldehyde was estimated by the bisulphite method; these gave the figures 5·6% and 11·17% for formaldehyde and total aldehyde respectively.

The bisulphite and iodometric methods were tested with Merck's pure formaldehyde solution and comparative experiments showed that the results obtained by the latter one were more uncertain and variable. Smith (*J. Amer. Chem. Soc.*, 1903, **25**, 1036) has reviewed the existing process for the estimation of formalehyde and recommends the use of the iodometric and cyanide methods for the estimation of formalehyde whilst the cyanide method is stated by Romijn to give correct figures for formaldehyde in presence of other aldehydes. No work appears to have been done on the estimation of formaldehyde in presence of acrolein; if iodometric method be adopted, the latter produces additional error by its absorption of iodine at the unsaturated bond. The latter method is, according to our experience, defective even in the case of formaldehyde and other saturated lower aldehydes as we observed in each case the formation of iodoform, while the calculation is based on the theory that the aldehyde is quantitatively transformed into the corresponding acid. In the case of acrolein, too, we observed the formation of iodoform so that it will be a second source of error.

The cyanide method and the bisulphite method were then tested and comparative experiments with pure formaldehyde solution showed that the former always gave low results with reference to those obtained by the latter. As no other process could help us in these estimations we adopted it, but evidently the results do not represent the actual picture. Further work in this line and the study of the conditions under which the successive stages of formaldehyde, acrolein and glyceric aldehyde can be individually and exclusively realised are in progress.

Examination of the gaseous products.—A mixture of mercuric chloride (5·55 g.) and glycerol (5·5 c.c.) was heated in an oil-bath at 180°—182°. The gaseous products were passed through 3

wash bottles containing successively Schiff's reagent, silver nitrate and lime-water. Pink colouration developed in the first bottle, which gradually intensified as the reaction proceeded; in the second, the liquid became slightly turbid, while the third one remained unaffected. It was noticed that almost all the gases evolved were absorbed in the first bottle and the rest in the second, while no bubbles appeared in the third. In the subsequent experiment, in order to ensure whether any carbon dioxide was formed or not, the arrangement of absorption-bottles was reversed: the first one contained lime-water. It was found that there was no turbidity which conclusively showed that carbon dioxide was not formed in the reaction and aldehydes were the main products.

In order to examine the absorbed aldehyde, the experiment was repeated by taking 5·4912 gm. of mercuric chloride and 6·930 gm. of glycerol using special type of wash-bottles in which the dipping tubes were connected with small funnels to ensure complete absorption and to prevent back suction of the liquid into the reaction flask. The wash-bottles in this experiment contained simply water. The liquid, after the reaction was complete, was examined for aldehydes after making it up to 250 c.c. The following tests were applied.

For formaldehyde.—(*a*) Two drops were diluted to 100 c. c. and to this mixture were added 2 c. c. of 1% solution of phenylhydrazine hydrochloride and 1 c.c. of a 5% solution of potassium ferrocyanide and then a few drops of concentrated hydrochloric acid when a red colouration developed showing exclusively the presence of formaldehyde. This very delicate test was then applied to a pure solution of acrolein prepared especially for the purpose, but no colouration was obtained.

(*b*) A solution of 1 g. of resorcinol in 3 c.c. of 25% caustic soda was prepared and to it a drop of the stock solution was added; a faint red colouration developed showing also the presence of formaldehyde.

For acrolein.—A concentrated solution of the absorbed gases was cooled by ice; hydrochloric acid gas was then passed through it when oily drops appeared. After 1 hour the oil was separated, washed with dilute sodium carbonate solution and taken up by ether. The ethereal solution was dehydrated and then evaporated; an oil was obtained having b.p. 125—129° (β-chloropropionic aldehyde boils at 125—130°). This showed the presence of acrolein. The residual

liquor was neutralised by sodium carbonate and was examined; it was found to contain formaldehyde.

Estimation of total aldehydes.—50 C.c. of a standard sodium bisulphite solution were added to 25 c.c. of the stock solution in a flask well corked and kept for 15 minutes; during this time a blank was performed against $N/10$-iodine.

Found: Total aldehydes in 250 c.c. stock calculated as CH_2O= 0·7735. Hence total aldehydes calculated as CH_2O on the amount of glycerol=11·17%.

The amount of formaldehyde in 250 c.c. stock solution by the cyanide method was found to be 0·385 gm. Hence formaldehyde= 5·6% on the amount of glycerol taken.

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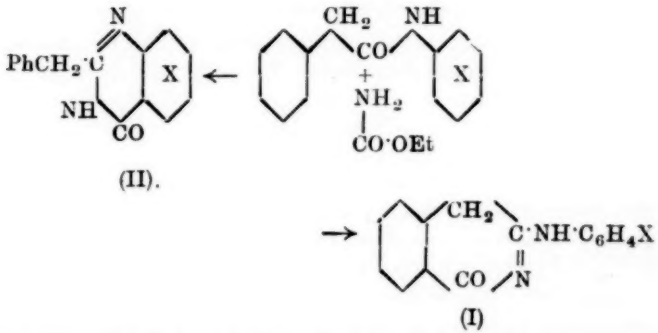
A New Synthesis of Quinazolines. Part II.

By Joti Sarup Aggarwal, Ram Saran Das and Jnanendra nath Ray.

In Part I of this investigation (*J. Indian Chem. Soc.*, 1929, **6**, 297) proof has been adduced that when ethyl carbamate condenses with an acylamine ($RCO{\cdot}NH{\cdot}C_6H_4X$) 4-oxyquinazolines are formed, sometimes in good yield, depending on the nature of R and the substituent X in the aromatic nucleus. The present investigation arose out of the fact that it seemed probable that if R is $PhCH_2$, there may be a chance of an *iso*quinoline (I) ring-formation. In view of the fact that so few methods are available for the synthesis of *iso*quinoline derivatives, it seemed of interest to explore this possibility.



(II).

(I)

The ring may also close in the alternative direction to give a benzyl quinazoline (II). Since a methyl group or a part of it directs substitution to a greater extent to the *ortho*-position than NH_2 or NH, the probability was an *iso*quinoline would be formed. If the product is an *iso*quinoline derivative it would have very feeble basic property or none at all, whilst if the product is a quinazoline the substance would show the usual basicity of the series. On actual experiment we find that it is a quinazoline that is formed and inspite of thorough search we failed to locate any *iso*quinoline derivative in the product. The investigation was continued because the quinazolines have an intrinsic interest of their own ; besides the quarternary salts of a few have been found by Gabriel and Colmann (D. R.-P. 161401) to have a lowering effect on the blood pressure.

The conditions of experiment are approximately the same as found by Bhattacharya, Bose and Ray (*J. Indian Chem. Soc.*, 1929, **6**, 279) but the yields are not satisfactory.

Starting substance.	Percentage yield of the quinazoline.
Phenaceto-anilide	8·5
Phenaceto-*o*-toluidide	3·0
Phenaceto-*m*-toluidide	9·0
Phenaceto-*p*-toluidide	7·2
Phenaceto-*o*-anisidide	13·0
Phenaceto-*p*-anisidide	10·2
Phenaceto-*o*-xylidide	2·8
Phenaceto-α-naphthalide	36·7
Phenaceto-β-naphthalide	31·4

These quinazolines give well-defined monomethyl derivatives when they are treated with methyl iodide and 2·8 % potassium hydroxide solution. These according to Bogert and Seil (*J. Amer. Chem. Soc.*, 1907, **29**, 534) are *N*-methyl derivatives.

In the next paper we will describe some further condensation products derived from the form II.

Experimental.

The following phenacetyl derivatives of aromatic amines used in this investigation do not appear to have been described before. The general method of preparation has been to heat phenylacetic acid (1 mol.), the amine (1 mol.) with a few drops of pyridine in an oil-bath at 160°-170°. The cooled product after treatment with dilute hydrochloric acid is usually crystallised from alcohol or from other suitable solvents.

Phenacetyl derivative, $C_6H_5 \cdot CH_2 \cdot CO \cdot NHR$.

Quantity of phenylacetic acid.	Quantity of amine.	M.p. of product		Analysis: P. c. of N. Found.	Calc.
14 gm.	10 gm.	*m*-toluidine.	75°. needles	6·32	6·20
13	12 ,,	*o*-anisidine.	84°	5·82	5·80
13	12 ,,	*p*-anisidine.	124°	5·94	5·80
13·6	14·3 ,,	α-naphthalide	175°.	5·39	5·36
13·6	14·3 ,,	β-naphthalide.	158°.	5·43	5·36
13·6	12·1 ,,	*o*-xylidide.	158°.	5·97	5·85

Condensation of Phenacetoanilide with Ethyl Carbamate : Formation of 2-Benzyl-4-oxyquinazoline (*Formula* I).—Phenacetoanilide (7 g.), ethyl carbamate (6 g.) and phosphoric oxide (20 g.) were thoroughly mixed in a flask and to the mixture 30 c.c. of xylene were introduced. The reaction was completed by heating in an oil-bath at 130°-140° for 3 hours. The xylene solution was freed from the solids and to the cold mixture water containing about 2 c.c. of hydrochloric acid was introduced. The resulting solution was filtered and carefully neutralised. The precipitated solids were collected and crystallised from hot absolute alcohol in beautiful plates ; m.p. 247°. The substance is soluble in alcohol, alkali and also in dilute acids. (Found : N, 11·90. $C_{15}H_{12}ON_2$ requires N, 11·86 per cent.).

2-Benzyl-3-methyl-4-quinazolone.—The preceding substance (0·8 g.) was dissolved in 15 c.c. of 2·8% solution of potassium hydroxide in methyl alcohol and the solution refluxed with methyl iodide (10 c.c.) on the water-bath for 6 hours. The product was then evaporated to dryness, and the residue was washed well with dilute alkali. The substance was crystallised in beautiful, small, colourless needles from dilute alcohol with the aid of animal charcoal. Yield 0·4 gm., m. p. 95°. (Found : N, 11·32. $C_{16}H_{14}ON_2$ requires N, 11·20 per cent.).

The *picrate* crystallised out of ethyl alcohol as yellow, silky needles, m. p. 170°.

Condensation of Phenaceto-o-toluidide with Ethyl Carbamate: Formation of 2-Benzyl-8-methyl-4-oxyquinazoline.

Phenaceto-*o*-toluidide (7·5 g.), ethyl carbamate (6 g.) and phosphoric oxide (20 g.) were thoroughly mixed in a flask and to the mixture 30 c. c. of xylene were introduced. The mixture was heated on the oil-bath at 140° for 3 hours. The quinazoline was isolated just as in the case of 2-benzyl-4-oxyquinazoline. On crystallisation from absolute alcohol it was obtained in slightly yellowish plates, m. p. 198°. The substance is soluble in alcohol, alkali and also in dilute acids. (Found : N, 11·08. $C_{16}H_{14}ON_2$ requires N, 11·2 per cent.).

The *picrate* of the above quinazoline was prepared, by mixing saturated solutions of the quinazoline and picric acid in absolute alcohol. Recrystallisation of the product from dilute alcohol gave beautiful, yellow, silky needles, m. p. 153°.

*Condensation of Phenaceto-*m*-toluidide with Ethyl Carbamate: Formation of 2-Benzyl-7-methyl-4-oxyquinazoline.*

A mixture of phenaceto-*m*-toluidide (7·5 g.) ethyl carbamate (6 g.), phosphoric oxide (20 g.) and xylene (35 c. c.) was heated on the oil-bath for 3 hours at 130-140° and the product was isolated as usual. The quinazoline was obtained in colourless plates on crystallisation from absolute alcohol, m. p. 230°. The substance is soluble in alcohol, alkali and also in dilute acids. (Found: N, 11·27. $C_{16}H_{14}ON_2$ requires N, 11·20 per cent.).

The *picrate* of the above quinazoline, prepared in the usual manner, was obtained in yellow, silky needles on crystallisation from alcohol; m. p. 168°. (Found: N, 14·81. $C_{22}H_{17}O_8N_5$ requires N, 14·61 per cent.).

*Condensation of Phenaceto-*p*-toluidide with Ethyl Carbamate: Formation of 2-Benzyl-6-methyl-4-oxyquinazoline.*

The substance was prepared by heating a mixture of phenaceto-*p*-toluidide (7·5 g.), ethyl carbamate (6 g.), phosphoric oxide (20 g.) and xylene (35 c. c.) on the oil-bath at 130—140° for 3 hours. The product was isolated in the usual way. When crystallised from absolute alcohol it was obtained in colourless plates, m. p. 239°. (Found: N, 11·16. $C_{16}H_{14}ON_2$ requires N, 11·2 per cent.).

2-Benzyl-3:6-dimethyl-4-quinazolone.—This was prepared exactly in the same way as 2-benzyl-3-methyl-4-quinazolone. The product was recrystallised from dilute alcohol with the aid of animal charcoal when colourless small needles, m. p. 116°, were obtained. (Found: N, 10·74. $C_{17}H_{16}ON_2$ requires N, 10·60 per cent.).

The *picrate* was obtained in the same way as that of 2-benzyl-6-methyl-4-quinazoline. It had m. p. 194° after crystallisation from alcohol. (Found: N, 14·53. $C_{22}H_{17}O_8N_5$ requires N, 14·61 per cent.).

*Condensation of Phenaceto-*p*-anisidide with Ethyl Carbamate: Formation of 2-Benzyl-6-methoxy-4-oxyquinazoline.*

Phenaceto-*p*-anisidide (8 g.), ethyl carbamate (6 g.), phosphoric oxide (20 g.) and xylene (35 c. c.) were well mixed in a flask and heated for 3 hours at 130-140° and the product was isolated as usual. On crystallisation from alcohol the above quinazoline was obtained

in colourless plates, m. p. 241°. (Found: N, 10·62. $C_{16}H_{14}O_2N_2$ requires N, 10·52 per cent.).

2-Benzyl-3-methyl-6-methoxy-4-quinazolone.

One gm. of the preceding substance was dissolved in 15 c. c. of 2· % solution of caustic potash in methyl alcohol and the solution was refluxed with 1 c. c. of methyl iodide for 6 hours. The product was isolated and crystallised from dilute alcohol with the aid of animal charcoal ; colourless needles, m. p. 121°. (Found: N, 10·07. $C_{17}H_{16}O_2N_2$ requires N, 10·00 per cent.).

The *picrate* was obtained in the usual way in yellow, silky needles, m. p. 198°. (Found: N, 14·26. $C_{22}H_{17}O_9N_5$ requires N, 14·14 per cent.).

Condensation of Phenaceto-o-anisidide with Ethyl Carbamate: Formation of 2-Benzyl-8-methoxy-4-oxyquinazoline.

The substance was obtained by heating a mixture of phenaceto-*o*-anisidide (8 g.), ethyl carbamate (6 g.), phosphoric oxide (20 g.), and xylene (35 c. c.) for 3 hours at 130-140°. The product was isolated as usual. On crystallisation from absolute alcohol it was obtained in colourless plates, m. p. 257°. (Found: N, 10·54. $C_{16}H_{14}O_2N_2$ requires N, 10·52 per cent.).

2-Benzyl-3-methyl-8-methoxy-4-quinazolone was prepared and isolated as usual. On crystallisation from dilute alcohol with the aid of animal charcoal, colourless needles, m. p. 138°, were obtained. (Found: N, 10·23. $C_{17}H_{16}O_2N_2$ requires N, 10·00 per cent.)

The *picrate* was prepared by the usual method; yellow, silky needles from absolute alcohol, m. p. 191°. (Found: N, 14·35. $C_{22}H_{17}O_9N_5$ requires N, 14·14 per cent.).

Condensation of Phenaceto-o-xylidide with Ethyl Carbamate: Formation of 2-Benzyl-7:8-dimethyl-4-oxyquinazoline.

Phenaceto-*o*-xylidide (8 g.), ethyl carbamate (6 g.), phosphoric oxide (20 g.) and xylene (35 c. c.) were heated at 130-140° for three hours, and the product obtained as before. On crystallisation from absolute alcohol, colourless plates melting at 189° were obtained. (Found: N, 10·71. $C_{17}H_{16}ON_2$ requires N, 10·60 per cent.).

The *picrate* of the preceding quinazoline was isolated as before and was obtained in yellow needles from alcohol, m. p. 165°. (Found: N, 14·39. $C_{23}H_{19}O_8N_5$ requires N, 14·2 per cent.).

Condensation of Phenaceto-α-naphthalide with Ethyl Carbamate: Formation of 2-Benzyl-7:8-benzo-4-oxyquinazoline.

A mixture of phenaceto-α-naphthalide (9 g.), ethyl carbamate (6 g.), phosphoric oxide (20 g.) and xylene (35 c. c.) was heated for three hours at 130-135°. The quinazoline came down by the addition of ice-cold water to the cold reaction mixture. Colourless crystals of the substance were obtained from pyridine, m. p. 265°. (Found: N, 9·91. $C_{19}H_{14}ON_2$ requires N, 9·79 per cent.).

Condensation of Phenaceto-β-naphthalide with Ethyl Carbamate: Formation of 2-Benzyl-6:7- or 5:6-benzo-4-oxyquinazoline.

A mixture of phenaceto-β-naphthalide (9 g.), ethyl carbamate (6 g.), phosphoric oxide (20 g.) and xylene (35 c. c.) was heated for 3 hours at 130-135°. The product was isolated by the addition of water to the cold solid reaction mixture. On crystallisation from pyridine, the substance was obtained in crystalline form, m. p. 278°. (Found: N, 10·02. $C_{19}H_{14}ON_2$ requires N, 9·79 per cent.).

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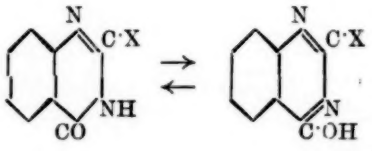
A New Synthesis of Quinazolines. Part III. Synthesis of 3 : 4-Quinazoloneylquinazolines.

By Joti Sarup Aggarwal and Jnanendra Nath Ray.

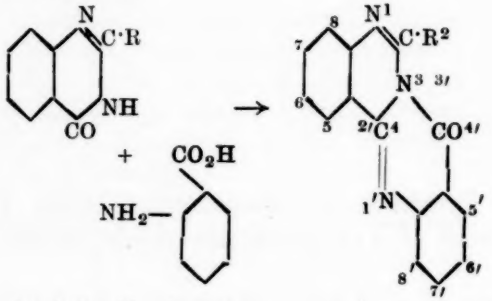
In Parts I and II of this investigation it has been established that when ethyl carbamate condenses with acylamines, 4-oxyquinazolines are formed. In Part II of this investigation we found evidence of the methylation products of these bodies to have an *N*-methyl structure, although the parent quinazolines were amphoteric substances dissolving with equal readiness in acids and alkalis. Therefore it was reasonable to suppose that an equilibrium existed between the two forms, and this can be represented as in the following typical case : –



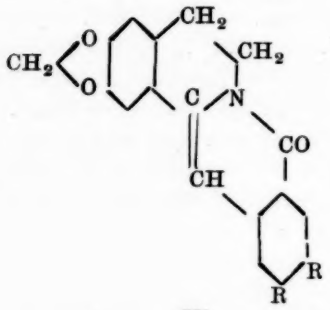
I. II.

Asahina, Manske and Robinson (*J. Chem. Soc.*, 1927, **131**, 1708) in their synthesis of rutaecarpin effected a condensation between a body containing the group —CO·NH— and anthranilic acid by means of phosphorous trichloride by the method of Sen and Ray (*J. Chem. Soc.*, 1926, **129**, 646) and encountered no difficulty in synthesising a quinazolone. Therefore it seemed possible to fuse a further quinazoline ring to the substance II in the position 3 : 4, if it really assumes this structure in its tautomerism. To test this point we condensed 2-phenyl-4-oxyquinazoline (*cf.* Bhattacharya, Bose and Ray, *J. Indian Chem. Soc.*, 1929, **6**, 297) with anthranilic

acid and we were able to isolate a product which clearly has the constitution (III).



III.



IV.

This substance (III) is, therefore, a 3:4-quinazoloneylquinazoline. The physiological activity of rutaecarpin is partly due to the presence of a quinazoline ring-system in the molecule; therefore it seemed of interest to synthesise these bodies with two such fused rings in the molecules. Further interest in these compounds lies in the fact that these bodies may be looked upon as analogous to oxyberberine (IV) in which two *N*-atoms in position 1 and 1′ of the former are replaced by two carbon atoms in the latter. Since it is quite common to find such replacement in natural products, therefo re it is not unlikely that probably substances derived from (III) will ultimately be found in nature and therefore we place on record our observations as to the colour reactions of these substances in the experimental part. It is worthy of note that the colour reactions given by these substances are very similar to that of the alkaloid rutaecarpin but not of oxyberberine.

Experimental.

Condensation of 2-Phenyl-4-oxyquinazoline with Anthranilic Acid: Formation of 2-Phenyl-3:4-quinazoloneylquinazoline (Formula III, R=C_6H_5).

A mixture of 2-phenyl-4-oxyquinazoline (1 g.), anthranilic acid (1 g.) and phosphorus trichloride (10 c.c.) was heated under reflux in a distillation flask for four hours. The excess of phosphorus trichloride was then removed by distillation. The residue was decomposed with ice. The solid collected and heated on the water-bath with 50 c.c. of hydrochloric acid (1:1) and the solution filtered. Unchanged starting material was recovered from the solution. The brown residue crystallised from absolute alcohol in lemon-yellow needles, m.p. 241-242°. Yield, 0·3 gm. (Found: C, 77·69; H, 4·25; N, 13·05. $C_{21}H_{13}ON_3$ requires C, 78·01; H, 4·02; N, 13·00 per cent.).

The colourless solution of the substance in acetic acid exhibits a slight bluish-green fluorescence after introduction of a few drops of sulphuric acid. The faint yellow solution in sulphuric acid becomes brownish on the addition of Mandeline's reagent which on standing turns yellowish green. The hot alcoholic solution becomes light yellow on the addition of solid caustic potash but after dilution with water the colour is discharged. A solution of the substance in 50% sulphuric acid and a trace of nitric acid remains unchanged on dilution (*cf.* oxyberberine).

Condensation of 2:7-Dimethyl-4-oxyquinazoline with Anthranilic Acid: Formation of 2:7-Dimethyl-3:4-quinazoloneylquinazoline.

A mixture of 2:7-dimethyl-4-oxyquinazoline (1 g.), anthranilic acid (2 g.) and phosphorus trichloride (10 c.c.) was refluxed on the water-bath for four hours. After the removal of the excess of phosphorus trichloride, the residue was decomposed with ice and ground with 50 c.c. of cold hydrochloric acid (1:1). The free quinazoline (starting substance) was recovered from the solution. The brown residue crystallised in yellow needles from absolute alcohol; m.p. above 285°. Yield, 0·3 gm. (Found: N, 15·31. $C_{17}H_{13}ON_3$ requires N, 15·27 per cent.).

The substance exhibits the bluish-green fluorescence with acetic acid and a drop of sulphuric acid, gives a brownish colour with Mandeline's reagent and light yellow colour with caustic potash in hot alcoholic solution as above but not the reaction of oxyberberine.

Condensation of 2-Methyl-6-methoxy-4-oxyquinazoline with Anthranilic Acid: Formation of 2-Methyl-6-methoxy-3:4-quinazoloneylquinazoline.

A mixture of 2-methyl-6-methoxy-4-oxyquinazoline (1 g.), anthranilic acid (2 g.) and phosphorus trichloride (10 c. c.) was heated under reflux for four hours. The dark brown residue, after usual treatment, was crystallised from absolute alcohol in yellowish-brown needles, m. p. 240° ; yield, 0·15 gm. (Found: N, 14·19. $C_{17}H_{13}O_2N_3$ requires N, 14·43 per cent.).

The substance gives the usual bluish-green fluorescence with acetic acid and a drop of sulphuric acid, a pale brownish colour with Mandeline's reagent and a light yellow colour with caustic potash in hot alcoholic solution.

Condensation of 2-Benzyl-4-oxyquinazoline with Anthranilic Acid: Formation of 2-Benzyl-3:4-quinazoloneylquinazoline.
(*Formula* III, R=$C_6H_5{\cdot}CH_2$)

2-Benzyl-4-oxyquinazoline (1 g.), anthranilic acid (1 g.) and phosphorus trichloride (10 c. c.) were thoroughly mixed and refluxed for four hours. After removal of the excess of phosphorus trichloride, the solid was decomposed with ice and heated on the water-bath with 50 c. c. of hydrochloric acid (1:1). The brownish-yellow product, on crystallisation from absolute alcohol, gave long, colourless, thin needles, m. p. 243-244°; yield, 0·25 gm. (Found: N, 12·40. $C_{22}H_{15}ON_3$ requires N, 12·46 per cent.).

It gives the bluish-green flourescence with acetic acid and a drop of sulphuric acid, a brownish colour with Mandeline's reagent and a light yellow colour with caustic potash in hot alcoholic solution.

Condensation of 2-Benzyl-7-methyl-4-oxyquinazoline with Anthranilic Acid: Formation of 2-Benzyl-7-methyl-3:4-quinazoloneyl-quinazoline.

A mixture of 2-benzyl-7-methyl-4-oxyquinazoline (1 g.), anthranilic acid (1 g.) and phosphorus trichloride (10 c. c.) was refluxed for four hours. The yellowish brown product obtained after removal of the excess of phosphorus trichloride and heating on the water-bath with 50 c. c. of hydrochloric acid (1:1) was crystallised from absolute alcohol in pale white needles, m. p. 213°; yield, 0·2 gm. (Found: N, 11·81. $C_{23}H_{17}ON_3$ requires N, 11·96 per cent.).

The substance gives slight bluish-green fluorescence with acetic acid and a drop of sulphuric acid, a brownish colour with Mandeline's reagent and the usual light yellow colour with caustic potash in alcoholic solution.

Condensation of 2-*Benzyl*-6-*methyl*-4-*oxyquinazoline with Anthranilic Acid*: *Formation of* 2-*Benzyl*-6-*methyl*-3:4-*quinazoloneylquinazoline*.

The quinazoline (1 g.) was thoroughly mixed with anthranilic acid (1 g.) and refluxed with phosphorus trichloride (10 c. c.) for four hours. The product after usual treatment was heated on the water-bath with 50 c. c. of hydrocholoric acid (1:1) and filtered. The brownish-yellow solid on crystallisation from alcohol gave colourless plates, m. p. 235—236°; yield, 0·25 gm. (Found: N; 12·13. $C_{23}H_{17}ON_3$ requires N, 11·96 per cent.).

The substance gives only slight bluish-green fluorescence with acetic acid and a drop of sulphuric acid, brown colour with Mandeline's reagent and a bright yellow colour with caustic potash in hot alcoholic solution.

Condensation of 2-*Benzyl*-8-*methoxy*-4-*oxyquinazoline with Anthranilic Acid*: *Formation of*-2-*Benzyl*-8-*methoxy*-3:4-*quinazoloneylquinazoline*.

The oxyquinazoline (1 g.) and anthranilic acid (1 g.) were thoroughly mixed and refluxed with phosphorus trichloride (10 c. c.). The product was isolated as usual. On crystallisation from absolute alcohol, colourless plates were obtained ; m. p. 254°; yield, 0·2 gm. (Found: N, 11·41. $C_{23}H_{17}O_2N_3$ requires N, 11·44 per cent.).

It exhibits slight bluish-green fluorescence with acetic acid and a drop of sulphuric acid, a brownish colour with Mandeline's reagent and a yellow colour with caustic potash in alcoholic solution.

Condensation of 2-*Benzyl*-6-*methoxy*-4-*oxyquinazoline with Anthranilic Acid*: *Formation of* 2-*Benzyl*-6-*methoxy*-3:4-*quinazoloneylquinazoline*.

A mixture of 2-benzyl-6-methoxy-4-oxyquinazoline (1 g.), anthranilic acid (1 g.) and phosphorus trichloride (10 c. c.) was refluxed for four hours. The brownish-yellow product, obtained after isolation in the usual way, gave white plates on crystallising from alcohol,

m. p. 244°. Yield, 0·2 gm. (Found: N, 11·31. $C_{23}H_{17}O_2N_3$ requires N, 11·44 per cent.).

A slight yellowish-green fluorescence with acetic acid and a drop of sulphuric acid, a brownish colour with Mandeline's reagent and a yellow colour with caustic potash in hot alcoholic solution are exhibited by the substance.

We wish to thank Prof. S. S. Bhatnagar for his kind interest in the work and one of us (J. S. A.) is indebted to the Punjab Chemical Research Trust for the award of the L. Harkishen Lal Scholarship which enabled him to take part in the investigation.

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Studies in Temperature Coefficients of some Photochemical Reactions in various Solvents in Dark and in Light.

By N. A. Yajnik and H. L. Uppal.

Dhar and his co-workers (*Z. Elektrochem.*, 1926, **32**, 586) have carried out a systematic study of temperature coefficients of a number of chemical reactions both photochemical and thermal.

In 1923 Dhar (*Z. anorg. Chem.*, 1923, **128**, 218) put forward the view that the temperature coefficient decreases with the increase in the order of reaction, that is, it is

(1) highest in case of zero-molecular,

(2) lower for unimolecular, and

(3) lowest for multimolecular reactions.

However the experimental data quoted by Dhar and his co-worker in support of this theory are probably not quite sufficient to justify a generalisation of this kind (also *cf.* von Halban, *Z. physikal. Chem.*, 1929, **67**, 129).

The von Halban-Dhar rule on account of the recent theories of catalysis and chemical reactions deserves a thorough investigation particularly with respect to the effect of the solvent on various reactants. It is also important to compare in every case the temperature coefficient of reactions both in the light and in the dark.

The present investigation was undertaken with the above mentioned points in view.

Experimental.

The following reactions were studied :—

(*a*) The oxidation of hydrogen sulphide by means of oxygen (in excess) in presence and in absence of light.

(*b*) Bromination of lactic acid in different solvents in dark and in presence of light (electric bulb 1,500 c. p.).

(*c*) Bromination of cinnamic acid in different solvents in absence and in presence of light.

Oxidation of Hydrogen Sulphide.

Salazor and Newman (*J. Chem. Soc.*, 1893, *ii*, **64**, 66) found the evidence of slight oxidation on keeping the solution of hydrogen sulphide in air. The aqueous solution is called " hydrogen sulphide water. " The solution is supposed to contain H° and HS' and S'' ions but the ionisation, $H_2S \rightarrow H^\circ + HS'$ is relatively much greater than $H_2S \rightarrow 2H^\circ + S''$.

Dilute solutions of hydrogen sulphide were prepared in distilled water. The reaction vessel used was a big boiling tube. As a result of a number of preliminary experiments it was noticed that the reaction is to a certain extent influenced by the catalytic effect of the walls of the vessel and that the reaction could best be studied by using an ordinary boiling tube. The tube was placed in a thermostat, the temperature of which was maintained constant within $\pm$ 0·1°.

It was found necessary to regulate the flow of oxygen. The proper flow of the gas was arrived at after a series of trials. The rate of reaction was measured iodometrically by taking out 5 c. c. of the solution from the reaction mixture at definite intervals of time.

TABLE I.

Oxidation of H_2S ($2H_2S + O_2 = 2H_2O + 2S$).

Temperature 20°.			Temperature 30°.			Temperature 40°.			
			Light.						
Time in minutes.	Concentration of H_2S in c.c. of $N/10$-$Na_2S_2O_3$.	Velocity constant. $k = 0{\cdot}4343K$.	Time in minutes.	Concentration of H_2S in c.c. of $N/10$-$Na_2S_2O_3$.	Velocity constant. $k = 0{\cdot}4343K$.	Time in minutes.	Concentration of H_2S in c.c. of $N/10$-$Na_2S_2O_3$.	Velocity constant. $k = 0{\cdot}4343K$.	Temperature coefficient.
0	2·30	—	0	2·02	—	0	2·07	—	
5	1·80	0·0212	5	1·62	0·0190	6	1·82	0·0150	$\frac{Kt+30}{Kt+20} = 0{\cdot}869$
10	1·30	0·0243	10	1·28	0·0198	10	1·48	0·0161	
16	1·00	0·0226	16	1·02	0·0197	15	1·22	0·0140	$\frac{Kt+40}{Kt+30} = 0{\cdot}856$
20	0·75	0·0211	20	0·80	0·0191	20	0·74	,,	
	Mean	0·0223	27	0·60	0·0198	35	0·50	0·0170	
				Mean	0·0194		Mean	0·0160	
			Dark.						
0	2·10	—	0	2·40	—	0	2·05	—	
5	2·00	0·0042	5	2·15	0·0095	5	1·75	0·0137	$\frac{Kt+30}{Kt+20} = 1{\cdot}37$
10	1·90	0·0048	10	2·05	0·0068	10	1·65	0·0091	
15	1·80	0·0044	18	1·80	0·0069	13	1·55	0·0093	$\frac{Kt+40}{Kt+30} = 1{\cdot}5$
24	1·65	,,	23	1·68	0·0068	20	1·35	0·0091	
	Mean	0·0044		Mean	0·0067		Mean	0·0092	

The temperature above 40° could not be tried as there was an appreciable loss of sulphuretted hydrogen even in dilute solutions at temperatures higher than 40°. The velocity constants were irregular and hence rejected.

Bromination of Lactic Acid.

Bromine reacts with lactic acid in light to give pyruvic acid according to the equation:

$$CH_3{\cdot}CH(OH){\cdot}CO_2H + Br_2 = CH_3{\cdot}CO{\cdot}CO_2H + 2HBr.$$

The reaction has also been worked out by Ghosh and Basu (*J. Indian Chem. Soc.*, 1925, **2**, 38) with the object of finding out how the velocity constant of photo-bromination varies with intensity, frequency and state of polarisation of incident light.

The rate of reaction was measured iodometrically as before. The light source was a 1,500 c. p. bulb placed at a distance of 12 cm. from the reaction vessel.

TABLE II.

Bromine (N/50) *and Lactic Acid* (N/50).

Solvent—Water.

Light.

Temperature 15°.			Temperature 25°.			
Time in minutes.	Concentration of Br_2 in c. c. of N/100-$Na_2S_2O_3$.	Velocity constant. $k=0{\cdot}4343K$.	Time in minutes.	Concentration of Br_2 in c. c. of N/100-$Na_2S_2O_3$.	Velocity constant. $k=0{\cdot}4343K$.	Temperature coefficient.
0	3·8	—	0	2·9	—	
5	3·4	0·0097	20	2·0	0·0080	
15	3·0	0·0069	25	1·9	0·0071	$\frac{Kt+25}{Kt+15}=1{\cdot}16$
20	2·8	0·0066	30	1·65	0·0080	
25	2·6	0·0062	35	1·6	0·0072	$\frac{Kt+35}{Kt+25}=1{\cdot}24$
30	2·3	0·0069	40	1·4	0·0080	
35	2·2	0·0068	45	1·2	0·0083	
	Mean	0·0066		Mean	0·0077	

Temperature 35°.			Temperature 45°.			
0	3·8	—	0	2·6	—	
5	3·4	0·0098	10	2·0	0·0114	
10	3·2	0·0100	15	1·7	0·0114	
15	3·0	0·0091	20	1·5	0·0123	$\frac{Kt+45}{Kt+35}=1{\cdot}19$
20	2·8	0·0095	25	1·4	0·0110	
25	2·4	0·0093	30	1·2	0·0112	
30	2·2	0·0093	35	1·1	0·0110	
	Mean	0·0095		Mean	0·0114	

TABLE III.

Bromine (N/50) *and Lactic Acid* (N/50.)

Solvent—Water.

Dark.

Temperature 15°.			Temperature 25°.			
Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$	Velocity constant. $k = 0{\cdot}4343K$.	Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$	Velocity constant $k = 0{\cdot}4343K$.	Temperature coefficient.
0	3·9	—	0	3·1	—	
5	3·7	0·0045	5	3·0	(0·0023)	
15	3·3	0·0044	10	2·8	0·0044	
22	3·1	0·0041	15	2·6	0·0043	$\frac{Kt+25}{Kt+15} = 1{\cdot}0$
32	2·8	0·0042	35	2·2	0·0042	
		Mean 0·0043			Mean 0·0043	

Temperature 35°.			Temperature 45°.			
0	4·45	—	0	3·4	—	
5	4·15	(0·0060)	5	3·0	(0·0108)	
10	4·05	0·0042	10	2·8	0·0084	$\frac{Kt+45}{Kt+35} = 1{\cdot}8$
15	3·75	0·0044	14	2·6	0·0079	
20	3·50	0·0047	17	2·5	0·0079	
25	3·35	0·0046	22	2·1	0·0081	
30	3·25	0·0047				
35	3·15	0·0048			Mean 0·0080	
		Mean 0·0045				

Results in the Dark.

The results in the dark are rather interesting. It would be clear from Table III (reaction velocity at 15°, 25° and 35° respectively) that velocity constant is same and does not increase with the rise in temperature. But the reaction proceeds with a greater velocity at 45°. Here the velocity is nearly double. The value of the temperature coefficient is 1·8.

Ghosh (*J. Indian Chem. Soc.*, 1925, **2**, 39) has also tried this reaction at 35° (dark). The velocity of reaction as found by him is much less than found here. We are unable to explain the difference although we have carefully repeated our results a number of times.

It may be mentioned that a bimolecular reaction velocity equation was tried but was not found to give as good a constant as the

monomolecular equation excepting in case of the reaction at 35° (dark), where the bimolecular equation also gave a fairly satisfactory constant.

TABLE IV.

Solvent—Chloroform.

Light.

Temperature 20°.			Temperature 30°.			
Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$	Velocity constant. $k=0{\cdot}4343K$.	Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$.	Velocity constant. $k=0{\cdot}4343K$.	Temperature coefficient.
0	5·2	—	0	3·00	—	
10	1·6	0·0511	7	0·90	0·0740	
13	1·2	0·0490	10	0·70	0·0630	$\frac{Kt+30}{Kt+20}=1{\cdot}35$
17	0·7	0·0510	12	0·40	0·0654	
20	0·4	0·0510	14	0·25	0·0720	
	Mean	0·0504	21	0·10	0·0700	
				Mean	0·0700	

Dark.

Temperature 20°.			Temperature 30°.			
0	0·60	—	0	0·80	—	
29	0·55	0·0013	13	0·70	0·0044	
60	0·50	0·0013	29	0·65	0·0031	$\frac{Kt+30}{Kt+20}=2{\cdot}35$
74	0·48	0·0013	50	0·55	0·0032	
87	0·45	0·0013	69	0·48	0·0032	
	Mean	0·0013		Mean	0·0034	

TABLE V.

Solvent—Carbon tetrachloride.

Temperature 20°.			Temperature 30°.			
			Light.			
Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$.	Velocity constant. $k = 0{\cdot}4343K$.	Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$.	Velocity constant. $k = 0{\cdot}4343K$.	Temperature coefficient.
0	2·20	—	0	6·6	—	
7	2·00	0·0059	34	3·5	0·0081	
12	1·90	0·0053	48	2·5	0·0087	$\frac{Kt+30}{Kt+20} = 1{\cdot}5$
20	1·70	0·0056	60	2·0	0·0086	
46	1·20	0·0057		Mean	0·0084	
Mean		0·0055				
			Dark.			
Temperature 20°.			Temperature 30°.			
0	2·25	—	0	2·0	—	
15	2·15	0·0013	14	1·80	0·0035	
23	2·10	0·0013	22	1·70	0·0032	$\frac{Kt+30}{Kt+20} = 2{\cdot}54$
50	1·90	0·0014	70	1·20	0·003	
Mean		0·0013	76	1·15	0·0034	
				Mean	0·0033	

TABLE VI.

Temperature Coefficients of the Reaction between Lactic acid and Bromine in different Solvents, Concentration N/50 each.

Light.			*Dark.*		
Solvent.	Temperature coefficient. $\frac{Kt+30}{Kt+20}$		Solvent.	Temperature coefficient. $\frac{Kt+30}{Kt+20}$	
Carbon tetrachloride	...	1·50	Carbon tetrachloride	...	2·58
Chloroform	...	1·35	Chloroform	...	2·35
Water	...	1·20	Water	...	1·80

The reaction was tried in carbon disulphide in light and in dark but it did not work.

Reaction between Bromine and Cinnamic Acid.

The reaction between bromine and cinnamic acid has been worked by Mathur, Gupta and Bhatnagar at one temperature (*Indian J. Phys.*, 1928, **2**, 243).

Ghose and Purkayastha (*J. Indian Chem. Soc.*, 1925, **2**, 261) have also studied this reaction in plane polarised, circularly polarised and ordinary light. The reaction proceeds fairly quickly in light but in dark the velocity is slow.

The velocity measurements were similarly carried on. The solvents tried were carbon disulphide, carbon tetrachloride, chloroform, ethyl acetate, ethyl bromide and ethyl formate.

It was found that in the dark the reaction is irregular in the beginning and also there is period of inhibition. So the two solutions of bromine and cinnamic acid after mixing were allowed to stand for half an hour and then the reaction velocity was measured.

Merck's pure bromine was used. Solutions of bromine and cinnamic acid were separately prepared in different solvents. Equimolecular solutions of both the reactants were used but it was found that reaction works according to unimolecular equations.

It may also be mentioned that Sudborough and Thomas (*J. Chem. Soc.*, 1910, **97**, 245C) have studied the reaction between equimolecular solutions of bromine and cinnamic acid in carbon tetrachloride at 15° in day light. They consider the reaction to be bimolecular but the values of the constant as calculated by them by the bimolecular equation vary from $4{\cdot}33 \times 10^{-2}$ to $7{\cdot}18 \times 10^{-2}$. Very much better constancy in the values can be obtained when their results are recalculated by the help of the unimolecular equation as shown below:—

$a = 26{\cdot}15$

t (hrs.).	$(a-x)$.	$\frac{1}{t}\cdot\frac{x}{a(a-x)}$.*	$\frac{1}{t}\log\frac{a}{a-x}$.
0·5	16·7	$4{\cdot}33 \times 10^{-2}$	0·389
1·0	12·7	$4{\cdot}05 \times 10^{-2}$	0·316
1·5	8·15	$5{\cdot}68 \times 10^{-2}$	0·387
2·0	5·5	$7{\cdot}18 \times 10^{-2}$	0·338

It is, therefore, evident that they were not justified in considering the reaction to be bimolecular.

* Sudborough and Thomas, *loc. cit.*

TABLE VII.

Bromination of Cinnamic Acid in Carbon Disulphide.

Bromine = N/30. Cinnamic acid = N/30.

Light.

Temperature 20°.			Temperature 30°.			
Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$.	Velocity constant $k = 0{\cdot}4343K$	Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$.	Velocity constant $k = 0{\cdot}4343K$	Temperature coefficient.
0	1·65	—	0	2·00	—	
10	0·95	0·0239	4	1·50	0·0301	
20	0·80	0·0157	8	1·10	0·0324	
28	0·60	0·0157	15	0·70	0·0304	$\frac{Kt+30}{Kt+20} = 1{\cdot}98$
37	0·45	0·0152	27	0.300	0·0300	
	Mean	0·0155		Mean	0·0305	

Dark.

Temperature 20°.			Temperature 30°.			
0	1·60	—	0	1·60	—	
10	1·40	0·0058	8	1·20	0·0156	
20	1·30	0·0045	15	0·90	0·0166	
29	1·20	0·0042	23	0·65	0·0177	$\frac{Kt+30}{Kt+20} = 3{\cdot}75$
30	1·05	0·0048	50	0·30	0·0165	
	Mean	0·0046		Mean	0·0164	

TABLE VIII.

Bromination of Cinnamic acid in Carbon Tetrachloride.

Bromine = N/30. Cinnamic acid = N/30.

Liyht.

Temperature 20°.			Temperature 30°.			Temperature 40°.			
Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$.	Velocity constant $k = 0{\cdot}4343K$	Time in minutes.	Concentration of Br_2 in c.c. of $N/100$ $Na_2S_2O_3$.	Velocity constant $k = 0{\cdot}4343K$	Time in minutes.	Concentration of Br_2 in c.c. of $N/100$ $Na_2S_2O_3$.	Velocity constant $k = 0{\cdot}4343K$	Temperature coefficient.
0	3·45	—	0	2·20	—	0	3·50	—	
9	2·70	0·0118	20	0·90	0·025	16	0·80	0·0405	$\frac{Kt+30}{Kt+20} = 1{\cdot}8$
16	2·20	0·0122	34	0·55	0·022	22	0·48	0·0401	
23	1·55	0·0151	46	0·32	0·020	27	0·20	0·0420	$\frac{Kt+40}{Kt+30} = 1{\cdot}8$
32	1·25	0·0130	53	0·15	0·024	37	0·10	0·0410	
40	1·00	0·0130							
61	0·70	0·0110		Mean	0 0227		Mean	0·0409	
	Mean	0·0126							

Dark.

Temperature 20°.			Temperature 30°.			
Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$.	Velocity constant. $k=0{\cdot}4343K$.	Time in minutes.	Concentration of Br_2 in c.c. of $N/100$-$Na_2S_2O_3$.	Velocity constant $k=0{\cdot}4343K$.	Temperature coefficient
0	4·00	—	0	2·60	—	
30	3·60	0·0015	34	2·45	0·0047	
45	3·40	0·0015	40	2·30	0·0048	$\frac{Kt+30}{Kt+20}=3{\cdot}6$
60	3·35	0·0013	47	2·10	0·0050	
75	3·30	0·0013	54	1·95	0·0049	
	Mean	0·0014		Mean	0·0049	

TABLE IX.

Bromination of Cinnamic Acid in Chloroform.

Bromine = N/30. Cinnamic acid = N/30.

Light.

Temperature 20°.			Temperature 30°.			Temperature 40°.			
Time in minutes.	Concentration of Br_2 in c.c. of $N/500$ $Na_2S_2O_3$.	Velocity constant $k=0{\cdot}4343K$.	Time in minutes.	Concentration of Br_2 in c.c. of $N/100$ $Na_2S_2O_3$	Velocity constant. $k=0{\cdot}4346K$.	Time in minutes.	Concentration of Br_2 in c.c. of $N/100$ $Na_2S_2O_3$.	Velocity constant. $k=0{\cdot}1343K$.	Temp. coefficient.
0	4·80	—	0	5·00	—	0	4·40	—	
14	4·60	0·0013	20	4·40	0·0027	21	3·55	0·0044	$\frac{Kt+30}{Kt+20}=1{\cdot}72$
24	4·50	0·0012	33	4·10	0·6026	32	3·20	0·0043	
43	4·05	0·0017	45	3·75	0·0027	62	2·40	0·0042	$\frac{Kt+40}{Kt+30}=1{\cdot}72$
51	3·95	0·0016	62	3·55	0·0024		Mean	0·0043	
	Mean	0·0015	70	3·35	Mean 0·0026				

Dark.

Temperature 26°.			Temperature 30°.		
0	3·60	—	0	2·40	—
22	3·50	0·00056	39	2·00	0·0020
46	3·40	0·00054	57	1·90	0·0019
86	3·20	0·00059	62	1·82	0·0020
	Mean	0·00056	80	1·75	0·0020
				Mean	0·0019

$\frac{Kt+30}{Kt+20}=3{\cdot}5$

TABLE X.

Reaction in Light.

Reactants.	Solvent.	Dielectric constant.	Temperature.	Velocity constant.	Temperature coefficient.
Lactic acid and bromine.	Water.	81	15°	0·0066	1·15
			25°	0·0077	1·24
			35°	0·0095	1·19
			45°	0·0114	
	Chloroform.	5·14	20°	0·0504	1·35
			30°	0·0700	
	Carbon tetrachloride.	2·25	20°	0·0055	1·50
			30°	0·0084	
Cinnamic acid and bromine.	Chloroform.	5·14	20°	0·0015	1·72
			30°	0·0026	1·72
			40°	0·0043	
	Carbon tetrachloride.	2·25	20°	0·0126	1·81
			30°	0·0227	1·82
			40°	0·0410	
	Carbon disulphide.	2·61	20°	0·0155	1·98
			30°	0·0300	

TABLE XI.

Reaction in Dark.

Reactants.	Solvents.	Dielectric constant.	Temperature.	Velocity constant.	Temperature coefficient.
Bromine and lactic acid.	Water.	81	15°	0·0043	1·80
			25°	0·0043	
			35°	0·0045	
			45°	0·0080	
	Chloroform.	5·14	20°	0·0013	2·61
			30°	0·0034	
	Carbon tetrachloride.	2·25	20°	0·0013	2·54
			30°	0·0033	
Bromine and cinnamic acid.	Chloroform.	5·14	20°	0·0005	3·50
			30°	0·0019	
	Carbon tetrachloride.	2·25	20°	0·0013	3·60
			30°	0·0048	
	Carbon disulphide.	2·61	20°	0·0045	3·75
			30°	0·0165	

TABLE XII.

Bromination of Cinnamic Acid and Lactic Acid.

Relation between Velocity Constant and Dielectric Constant.

Solvent.	Dielectric constant.	Velocity constant at 20°.	
		Lactic acid.	Cinnamic acid.
Carbon tetrachloride.	2·25	0·0500	0·0014
Carbon disulphide.	2·61	—	0·0431
Chloroform.	5·14	0·0095	0·0190
Water.	81·00	0·0066	Not tried.

From the above table it is clear that there can be no possibility of any relationship between the dielectric constant and velocity constant.

These results are in agreement with the results of Mathur, Gupta and Bhatnagar (*loc. cit.*) on the bromination of cinnamic acid in various media. These are further supported by the work of Oliver (*Rec. trav. chim.*, 1916, **36**, 117) on acid chlorides of benzene sulphonic acid derivatives in various solvents and also by Matthew and Williamson (*J. Amer. Chem. Soc.*, 1923, **45**, 2577) who have observed that the isomeric change of acetyl chloraminobenzene into *p*-chloracetanilide under the influence of ultra-violet rays is more rapid in ethyl alcohol than either in benzene or acetic acid, but the dielectric constant increases in the order:—

Benzene: Acetic acid: Alcohol.

The halogen acetic acids are decomposed by light (Enter, *Ber.*, 1915, **49**, 1366) more rapidly in ether than in benzene but the dielectric constant of benzene is lower than that of ether.

The changes of certain leuco-derivatives of the triphenyl methane series under the influence of ultra-violet rays were studied by Lifschitz and Joffee (*Z. physikal. Chem.*, 1921, **97**, 426). They have observed the reaction to proceed more rapidly in ethyl alcohol than in ether or benzene and here again the dielectric constant of alcohol is much higher than either of ether or benzene.

From the above it is clear that there exists no direct relationship between the velocity constant and dielectric constant.

In the following table the temperature coefficients and the dielectric constant of the solvents have been assembled together.

TABLE XIII.

Relation between Temperature Coefficient and Dielectric Constant.

Solvent.	Dielectric constant.	Bromination of cinnamic acid.		Bromination of lactic acid.	
		Light.	*Dark.*	*Light.*	*Dark.*
Carbon tetrachloride.	2·25	1·80	3·60	1·50	2·58
Carbon disulphide.	2·61	1·98	3·75	...	...
Chloroform.	5·14	1·72	3·50	1·35	2·35
Water.	81	...	...	1·20	1·80

Bromination of Cinnamic Acid.

From the above tables it is clear that the solvents can be arranged as follows according to the values of temperature coefficient as obtained experimentally:—

Carbon disulphide: Carbon tetrachloride: Chloroform.

Taking into consideration the influence of dielectric constant the order should be:—

Carbon tetrachloride: Carbon disulphide: Chloroform.

Thus it is seen that the order of the temperature coefficient found experimentally does not show any relationship with the dielectric constant.

Similarly in the case of investigations on the bromination of lactic acid no definite relationship between the temperature coefficients and the dielectric constants of the media is found to hold good.

The authors would like to take this opportunity of thanking Dr. S. S. Bhatnagar for valuable help given by him during the course of this investigation.

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The Dielectric Constant of Binary Mixtures. Part II. Alcohols in Benzene.

By P. C. Mahanti.

In Part I (*J. Indian Chem. Soc.*, 1929, **6**, 411) the results of calculation of electric moments and the measurements of dielectric constant of some organic liquids whose molecules do not react upon those of benzene, have been presented and the molecular polarisation has been treated as a function of concentration of the binary mixture, the relationship being given by a linear law. But in the case of associated molecules, this linear law is found not to hold good. It is, therefore, of interest to verify Debye's law experimentally in the case of such molecules. The alcohols have been chosen for the purpose. Besides it has been observed in a previous paper (*Indian J. Phys.*, 1929, **3**, 467) that so far as the normal primary alcohols are concerned they have practically the same electric moment, no matter whether the chain is long or short, open or closed. The *iso*-alcohols thus present another interesting point to be studied.

The apparatus used and the method of procedure are exactly the same as described in Part I. The only difference is that very dilute solutions have been used to avoid association of the molecules which generally takes place at higher concentrations. The chemicals used were brought from Kahlbaum. The same formulae have been used. Thus

$$P_A = \frac{P_{AB} - P_B C_B}{C_A} \qquad \ldots \qquad (1)$$

and also

$$P_A = \frac{4\pi}{3} N \left(\gamma_A + \frac{\mu^2}{3KT} \right)$$

$$= \frac{n_A^2 - 1}{n_A^2 + 2} \cdot \frac{M_A}{d_A} + \frac{4\pi}{3} N \cdot \frac{\mu^2}{3KT} \qquad \ldots \qquad (2)$$

Hence μ can be calculated for the solute molecule.

TABLE I.

Solute.	C_A.	d_{AB}.	ϵ_{AB}.	P_{AB}.
*iso*Propyl alcohol.	0·00	0·870	2·26	26·50
	7·21	0·864	2·58	30·60
	14·72	0·857	2·89	33·97
	16·98	0·854	3·01	35·20
	21·17	0·851	3·16	36·50
	24·76	0·848	3·46	38·96
	32·72	0·842	4·06	43·24
*iso*Butyl alcohol.	0·00	0·872	2·26	26·50
	3·06	0·868	2·38	28·25
	9·98	0·864	2·40	32·50
	15·30	0·860	2·62	36·24
	19·22	0·855	3·16	38·10
	23·17	0·853	3·38	40·11
	28·72	0·849	3·81	43·85
*iso*Amyl alcohol.	0·00	0·872	2·26	26·50
	4·38	0·866	2·44	29·25
	7·73	0·864	2·57	31·21
	11·47	0·862	2·72	33·50
	17·10	0·859	2·78	36·95
	22·82	0·853	3·24	40·30
	27·96	0·848	3·44	42·80
n-Undecyl alcohol.	0·00	0·872	2·26	22·46
	1·15	0·869	2·27	26·91
	2·17	0·866	2·32	28·25
	3·34	0·865	2·38	29·77
	5·29	0·864	2·44	31·09
	7·19	0·862	2·53	33·21
	9·62	0·859	2·65	35·85
	12·47	0·856	2·74	38·46
n-Dodecyl alcohol.	0·00	0·872	2·28	26·46
	0·63	0·871	2·23	26·74
	1·32	0·870	2·32	27·89
	2·90	0·868	2·35	29·00
	4·90	0·865	2·41	30·79
	7·56	0·861	2·53	33·99

TABLE I—contd.

Solute.	C_A.	d_{AB}.	ϵ_{AB}.	P_{AB}.
n-Dodecyl alcohol	9·98	0·858	2·62	36·28
	13·90	0·853	2·80	4.·96
n-Phenylethyl	0·00	0·872	2·26	26·46
alcohol.	1·66	0·873	2·32	27·56
	3·75	0·876	2·50	30·31
	5·44	0·884	2·65	32·28
	7·02	0·886	2·71	33·20
	9·09	0·889	2·80	34·59
	11·48	0·895	2·89	35·87
	13·74	0·898	2·95	36·87
n-Phenylpropyl	0·00	0·872	2·26	22·46
alcohol.	1·00	0·873	2·32	27·50
	2·38	0·876	2·50	29·30
	3·74	0·879	2·53	30·80
	5·20	0·882	2·62	32·22
	6·65	0·885	2·71	33·59
	8·96	0·888	2·80	35·13
	12·27	0·892	2·95	37·60

TABLE II.

Alcohols.	n_A	d_A	P_A	P''_A	P'_A	$\mu \times 10^{18}$
*iso*Propyl— $CH_3{\cdot}CH(OH)CH_3$	1·377	0·789	83	17·5	65·5	1·78
*iso*Butyl— $(CH_3)_2CH{\cdot}CH_2(OH)$	1·395	0·806	89	22·0	67·0	1·79
*iso*Amyl— $(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2(OH)$	1·407	0·810	95	26·8	68·2	1·82
n-Undecyl— $C_{11}H_{23}OH$.	1·441	0·833	112	55·6	57·4	1·66
n-Dodecyl— $C_{12}H_{25}OH$.	1·440	0·830	113	58·9	54·1	1·62
n-Phenylethyl— $C_6H_5{\cdot}CH_2{\cdot}CH_2OH$.	1·526	0·995	93	37·6	55·4	1·64
n-Phenylpropyl— $C_6H_5{\cdot}CH_2{\cdot}CH_2CH_2{\cdot}OH$.	1·525	0·990	97	42·1	54·9	1·63

Discussion.

The results clearly indicate that in *iso*-alcohols the carbon atoms associated with the CH-group have different binding forces leading to dipole-moments different in magnitude from those of the primary alcohols. It also seems that μ is larger when the carbon chain is branched as in the *iso*-alcohols. In the case of primary alcohols, the dipole-moment is found to be sensibly constant and the mean value can be taken as $1{\cdot}68 \times 10^{-18}$ whereas in the case of *iso*-alcohols, it is $1{\cdot}80 \times 10^{-18}$. This may be presumably explained as follows:—

Hydrocarbons in themselves are non-polar. The introduction of a polar group, such as the OH-radicle in this case, develops a dipole. It is, therefore, reasonable to assume that the displacement of the electrical charge which gives rise to the dipole takes place mainly in the radicle itself and in the part of the carbon adjacent to it. This means in turn that the magnitude of the dipole-moment is determined by the nature of the atoms in or near to the OH-group whereas the existence of non-polar groups at a greater distance has practically no effect on the dipole-moment.

Two aliphatic esters have been investigated by Krchma and Williams (*J. Amer. Chem. Soc.*, 1927, **49**, 2414). They have used carbon tetrachloride as the non-polar solvent. Their results are—

for methyl acetate, $\mu = 1{\cdot}67 \times 10^{-18}$
for ethyl acetate, $\mu = 1{\cdot}74 \times 10^{-18}$.

These two results agree between themselves but are rather different from those obtained for the aromatic esters. They are—

for methyl benzoate, $\mu = 2{\cdot}06 \times 10^{-18}$
for ethyl benzoate, $\mu = 2{\cdot}10 \times 10^{-18}$.

Hence the dipole-moment will be considerd as a property of the polar OH-group largely independent of the presence of other polar or non-polar groups.

Thus we notice that the dipole-moment is one of the most important properties closely related to the actual electrical structure of the molecules. It may here be remarked that for organic compounds the electrical structure is not so pronounced, and it has been

possible for the chemists to develop an elaborate theory of structural formulae without any consideration of their electrical properties. The electrical nature of inorganic compounds has been considered of primary importance not only from their behaviour in solutions but from various other considerations. It is now more or less certain that the ultimate constituents of matter are the protons and electrons and in organic compounds the forces which bind the different atoms in a molecule should be electrical in origin. The bond theory is still the fundamental basis of organic chemistry. In recent years, however, several electrical theories have been put forward in connection with structure of organic compounds. These theories, as a rule, are not based on electrical properties of the molecules but on their chemical behaviour. The author is of opinion that the dipole-moment of organic molecules can give a clue to the real nature of the bond theory regarding its electrical origin. This, however, will be treated separately elsewhere.

I beg to acknowledge my thanks to Mr. R. N. Das-Gupta, for helping me in taking the observations. My best thanks are also due to Prof. P. N. Ghosh, for helpful criticism and kind encouragement during the course of the investigation.

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Effect of Poisons on the Velocities of Dehydrogenation of (1) Methyl alcohol and (2) Formaldehyde at a Surface of Copper Catalyst Activated with Ceria as Promoter.

By J. C. Ghosh and Jagat Bandhu Bakshi.

In a previous paper (*J. Indian Chem. Soc.*, 1926, **3**, 415) the authors have shown that methyl alcohol can be dehydrogenated on the surface of copper catalyst prepared from copper acetate with thoria or ceria as promoters. These catalysts showed no diminution in activity when worked continuously for about 60 hours. The present investigation was carried out with the object of discovering how various poisonous substances mixed with methyl alcohol would affect the velocity of the following reactions on these catalytic surfaces.

$$CH_3{\cdot}OH \longrightarrow H{\cdot}CHO + H_2 \quad \ldots \quad (1)$$

$$H{\cdot}CHO \longrightarrow CO + H_2 \quad \ldots \quad (2)$$

In our previous experiments, the space velocity was very large and methyl alcohol vapour could come in contact with the active catalyst surface for a very short time so that though reaction (1) was almost complete, reaction (2) was almost completely suppressed.

In our present investigation, the experimental arrangement has been so modified that the velocities of reaction (1) and (2) could be separately determined and the influence of poisons on each of these can be studied quantitatively.

Experimental.

The experimental arrangement will be clear from Fig. 1. The reaction tube A was filled with 10 gm. cupric oxide with ceria as promoter and placed inside a vertical electric furnace B. The catalyst was reduced *in situ* by passing a current of pure hydrogen through the open ends C and D for 48 hours at about 180°. After the reduction is complete, the end D is sealed off and the catalyst allowed to cool down in an atmosphere of hydrogen. The reaction tube A is connected to a glass capillary manometer at the top. To prevent condensation of undecomposed methyl alcohol, electric heating coils were placed round the lower limb of the reaction tube

A and also round the capillary tube of the mercury manometer as shown in the diagram. A very small portion E of the capillary at the top was not covered with the heating coil so that the pressure required to bring the mercury meniscus to a certain level in this zone can be easily observed. Methyl alcohol, kept inside a

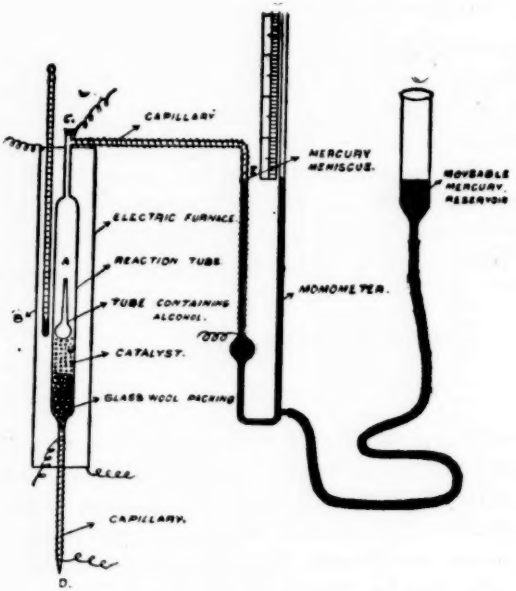

Fig. 1.

Hoffman's bottle, was dropped into the reaction vessel by opening the cork at C, which was closed immediately after. The temperature of the furnace was kept constant by regulating the electric current, and was noted by means of a long-stem thermometer whose bulb was at the centre of the furnace, close to the catalyst material.

Experiment No. 1.

No catalyst inside the reaction tube. Glass wool (Merck's guaranteed reagent) washed with pure water was substituted for catalyst.

Table I.

0·0346 Gm. of methyl alcohol was introduced.

Temp.	Time after dropping MeOH.	Excess pressure inside the reaction tube.
195°	1 min.	22·3 cm. (of Hg.)
	2 mins.	22·7
	3 mins.	22·7
	15 mins.	22·7

The experiment shows that within a minute after dropping methyl alcohol, the whole of the liquid is converted into vapour, and that the pressure remained steady after the evaporation is completed indicating that methyl alcohol vapour does not undergo any condensation inside the apparatus.

In later experiments with catalysts, it was assumed that methyl alcohol takes about a minute and a half for complete evaporation and the pressure P recorded at that time was taken to be the pressure of undecomposed methyl alcohol vapour. If both the reactions,

$$CH_3{\cdot}OH \longrightarrow H{\cdot}CHO + H_2 \quad \ldots \quad (1)$$

$$H{\cdot}CHO \longrightarrow CO + H_2 \quad \ldots \quad (2)$$

are monomolecular on the catalyst surface, then the velocity constants K_1 and K_2 can be easily calculated from the pressure recorded in the manometer. It is clear from the previous paper, that the second reaction takes place only after the first reaction has been almost completed. Obviously when the observed pressure is less than $2P$, we are dealing with the first decomposition ; and

P'_{t_1} (observed pressure at any time t_1)

$$= P(1-x'_{t_1}) + 2xt_1P \quad \ldots \quad (3)$$

$$P'_{t_2} = P(1-x'_{t_2}) + 2x'_{t_2}P \quad \ldots \quad (4)$$

where x'_{t_1} is the fraction of methyl alcohol decomposed at time t_1.

The velocity constant K_1

$$= \frac{1}{t_2-t_1} \log_e \frac{(1-x'_{t_1})}{(1-x'_{t_2})}$$

$$= \frac{1}{t_2-t_1} \log_e \frac{2P-P_{t_1}}{2P-P_{t_2}} \quad \ldots \quad (5)$$

Again when the observed pressure is greater than $2P$ but less than $3P$, reaction (2) is taking place, and

$$P''_{t'} = P + P(1-x''_{t'}) + 2x''_{t'}\,P \qquad \ldots \qquad (6)$$

$$P''_{t''} = P + P(1-x''_{t''}) + 2x''_{t''}\,P.$$

Where $x''_{t'}$ is the fraction of formaldehyde decomposed at time t'.

The velocity constant K_2

$$= \frac{1}{t''-t'} \log_e \frac{1-x''_{t'}}{1-x''_{t''}} = \frac{1}{t''-t'} \log_e \frac{3P-P''_{t'}}{3P-P''_{t''}} \qquad \ldots \qquad (7)$$

CATALYST No. 1.

Ten gm. of copper oxide with 0·1% ceria were prepared and reduced according to the method described in the previous paper. The temperature of the furnace was kept at 195°. The pressure due to the evaporation of pure methyl alcohol within 1½ min. after its introduction into the apparatus was 22·8 cm.

TABLE II.

$T = 195°$. $P = 22·8$ cm.

Time in mins.	t_1	t_1+10	t_1+15	t_1+20	t_1+25	t_1+30	t_1+35
Observed press.	27	31·2	33·1	34·8	36·1	37·3	38·6 cm.
K_1	—	0·0255	0·0264	0·0271	0·0266	0·0269	0·0278

For observed pressure greater than $2 \times 22·8$ cm.

Time in mins.	t'	$t'+6$	$t'+11$	$t'+16$	$t'+21$	$t'+26$	$t'+31$	$t'+36$
Observed press.	46·9	47·6	48·2	48·7	49·3	49·9	50·6	51·3 cm.
K_2	—	0·00552	0·00552	0·00552	0·00575	0·00575	0·00621	0·00621

It will be seen that the monomolecular velocity constants agree very well among themselves and that the velocity constant of dehydrogenation of methyl alcohol is about five times that of decomposition of formaldehyde.

Effect of Poison on Catalyst No. 1.

Poison—Carbon disulphide. Carbon disulphide was mixed with methyl alcohol, and this liquid mixture introduced into the apparatus.

TABLE III.

Weight of catalyst = 8 gm. as copper.

Weight of CS_2 absorbed by the catalyst = 0·00290 gm. P = 27·3 cm.

Time in mins.	t_1	t_1+5	t_1+10	t_1+15	t_1+25
Observed press.	30·6	34·3	36·8	39·2	43·5 cm.
K_1	—	0·0335	0·0299	0·0299	0·0312

For observed pressure greater than $2 \times 27{\cdot}3$ cm.

Time in mins.	t'	$t'+95$	$t'+125$	$t'+155$
Observed press.	63·3	67·5	68·1	69·1 cm.
K_2	—	0·00276	0·00289	0·00239

For very small addition of carbon disulphide, the velocity constant of dehydrogenation of methyl alcohol slightly increases whereas the velocity of decomposition of formaldehyde is almost halved.

TABLE IV.

Wt. of catalyst = 8 gm. as Cu.

Wt. of CS_2 absorbed by catalyst = 0·0230 gm. P = 18 cm.

Time in mins.	t_1	t_1+16	t_1+25	t_1+45	t_1+55
Observed press.	18·5	20·9	21·8	24·3	25·4 cm.
K_1	—	0·0092	0·00828	0·00897	0·0092
K_2	The value of K_2 is negligibly small.				

Complete poisoning is effected when 0·0329 gm. of carbon disulphide is added to this copper catalyst obtained by reduction of 10 gm. of CuO (8 gm. as Cu).

A series of similar experiments were carried out with double the amount of copper catalyst and it was found that for complete poisoning 0·0695 gm. of carbon disulphide was necessary. The diminution in velocity constant, as carbon disulphide was continually increased, was very similar to that observed in the previous case.

Poison—Carbon tetrachloride. Catalyst No. 2 was prepared as before. It should be noted, however, that the activity of a catalyst cannot exactly be reproduced, even though the method

of preparation is the same. It was necessary therefore to measure the velocity constants K_1 and K_2 for pure methyl alcohol for each fresh sample of catalyst.

TABLE V.

Temp. = 195°.

The values of K_1 and K_2 for pure methyl alcohol on the surface of catalyst No. 2 are 0·0253 and 0·00529 respectively and are slightly less than those for catalyst No. 1.

Wt. of catalyst = 8 gm. as Cu.

Wt. of poison (CCl_4) = 0·01212 gm. P = 19·4 cm.

Time in mins.	t_1	t_1+1	t_1+11	t_1+26	t_1+41	t_1+71	t_1+96
Observed press.	22·1	22·6	26·1	28·0	29·0	30·2	30·7 cm.
K_1	—	0·0299	0·0253	0·0184	0·0138	0·0092	0·00759

It is obvious that K_1 does not remain constant as in the case of carbon disulphide poisoning, but with time the poisoning effect becomes greater and greater and the velocity constant continually diminishes until it reaches a value about $\frac{1}{4}$ of the original value.

Complete poisoning is observed when 0·0241 gm. of carbon tetrachloride is added to 8 gm. of the copper catalyst.

TABLE VI.

Poison—Chloroform.

Catalyst No. 2. Temp. = 195°.

Wt. of poison (chloroform) = 0·01117 gm.

Wt. of catalyst = 8 gm. as Cu.

P (pressure of undecomposed methyl alcohol vapour) = 22·7 cm.

Time in mins.	t_1	t_1+5	t_1+13	t_1+23	t_1+33
Observed press.	24·8	29·8	35·2	39·8	43·0 cm.
K_1	—	0·0552	0·0552	0·0552	0·0622

TABLE IV—*continued*.

For observed pressure greater than $2P$.

Time in mins.	t'	$t'+45$	$t'+60$
Observed press.	48·1	50·7	51·0 cm.
K_2	—	0·00322	0·00253

With the addition of a small amount of chloroform, the velocity constant of dehydrogenation of methyl alcohol increased to about twice its original value, but the velocity constant of decomposition of formaldehyde showed a considerable falling off from the very beginning. The poisonous action of chloroform is different from that of carbon tetrachloride in that there is no progressive change in the values of the velocity constants with time.

TABLE VII.

Wt. of poison ($CHCl_3$) = 0·02209 gm.
Wt. of catalyst = 8 gm. as Cu.
Temp. = 195°. P = 19·8 cm.

Time in mins.	t_1	t_1+5	t_1+25	t_1+40	t_1+55
Observed press.	20·0	20·5	22·4	23·3	24·0 cm.
K_1	—	0·00529	0·00529	0·00460	0·00460

Poisoning was complete when 0·03263 gm. of chloroform was added to 8 gm. of the copper catalyst.

Poison—Acetonitrile. Catalyst No. 3 was prepared in a similar way as catalyst No. 1 or No. 2, but when tested with pure methyl alcohol, K_1 and K_2 at 195° were found to be 0·0598 and 0·00759 respectively.

TABLE VIII.

Wt. of poison (acetonitrile) = 0·00728 gm.
Wt. of catalyst = 8 gm. as Cu.
Temp. = 195°. P = 27·7 cm.

Time in mins.	t_1	t_1+5	t_1+15	t_1+25	t_1+40	t_1+60	t_1+95
Observed press.	31·5	33·7	35·5	36·6	37·6	38·2	39·0 cm.
K_1^2	—	0·0184	0·0115	0·0092	0·0069	0·0046	0·0039

As in the case of carbon tetrachloride the velocity constants continually diminishes indicating that it takes some time before the maximum effect of the poison is observed. Acetonitrile appears to be a very violent poison, the velocity constant decreasing about 15 times by the addition 0·00728 gm. of acetonitrile to 8 gm. of copper catalyst. Complete poisoning is effected with 0·0143 gm. of the poison.

Poison—Bromine. Catalyst No. 3 with K_1 and K_2 for pure methyl alcohol 0·0598 and 0·00759 respectively.

TABLE IX.

Wt. of poison (bromine) = 0·01878 gm.
Wt. of catalyst = 8 gm. as Cu.
Temp. = 195°. P = 22·6 cm.

Time in mins.	Observed press.	K_1	K_2
t_1	26·5 cm.	—	—
$t_1 + 20$	36·0	0·0345	—
$t_1 + 35$	39·2	0·0322	—
For observed pressure greater than $2P$.			
t'	46·1 cm.	—	—
$t' + 5$	46·3	—	0·00376

TABLE X.

Wt. of poison (bromine) = 0·1015 gm.
Temp. = 195°. P = 33·1 cm.

Time in mins.	Observed press.	K_1
t_1	36·6 cm.	—
$t_1 + 10$	41·9	0·01978
$t_1 + 25$	46·8	0·0213
$t_1 + 40$	50·7	0·0181

With the addition of bromine, the velocity constants K_1 and K_2 both diminish from the very beginning. The full effect for a given amount of poison is perceived immediately, as the velocity constants, in each experiment, are found to agree fairly well with one another,

Dehydrogenation of methyl alcohol stops completely when 0·1677 gm. of bromine is added to 8 gm. of the copper catalyst.

Effect of Iodine.—A large number of experiments were tried with increasing quantities, but no poisoning effect could be detected. In fact, the velocity constants K_1 and K_2 increase as will be clear from Table XI.

TABLE XI.

Wt. of iodine = 1·4715 gm.
Wt. of catalyst No. 3 = 8 gm. as Cu.
Temp. = 195°. P = 27·7 cm.

Time in mins.	Observed press.	K_1	K_2
t_1	34·9 cm.	—	—
t_1+2	38·5	0·0966	—
t_1+7	44·8	0·0943	—
For observed pressure greater than $2P$.			
t'	61 cm.	—	—
$t'+5$	62·3	—	0·01196
$t'+10$	63·5	—	0·01196

TABLE XII.

Poison—Mercuric iodide.

Wt. of HgI_2 = 0·00176 gm.
Wt. of catalyst No. 3 = 8 gm. as Cu.
Temp. = 195°. P = 39·3 cm.

Time in mins.	Observed press.	K_1	K_2'
t_1	43·5 cm.	—	—
t_1+7	54·9	0·0598	—
t_1+27	72·5	0·0644	—
For observed pressure greater than $2P$.			
t'	80·9 cm.	—	—
$t'+10$	84·9	—	0·0115
$t'+15$	86·8	—	0·0115

Addition of a very small amount of mercuric iodide does not affect the first dissociation velocity K_1 and considerably increases the second dissociation velocity K_2. With further addition of mercuric iodide the poisoning effect is easily noticeable.

TABLE XIIA.

Catalyst No. 3.

Wt. of HgI_2 = 0·00848 gm.
Wt. of catalyst = 8 gm. as Cu.
Temp. = 195°. P = 29 cm.

Time in mins.	Observed press.	K_1	K_2
t_1	35 cm.	—	—
$t_1 + 5$	39·4	0·039	—
$t_1 + 15$	46·0	0·0391	—
$t_1 + 30$	52·8	0·0414	—
For observed pressure greater than $2P$.			
t'	61 cm.		—
$t' + 15$	63·7		0·0069
$t' + 30$	66·3		0·00667

TABLE XIIB.

Wt. of HgI_2 = 0·01246 gm. P = 27·8 cm.

Time in mins.	Observed press.	K_1.
t_1	30·5 cm.	—
$t_1 + 10$	33·8	0·0126

With increased addition of poison, the velocity constants K_1 and K_2 both continue to diminish until for an addition of 0·01246 gm. of mercuric iodide to 8 gm. of the copper catalyst, the poisoning is complete. It should be noted here, that since iodine has no depressing effect on the velocity constants the inhibiting action observed here is due to mercury atoms only.

Discussion.

Taylor (*Proc. Roy. Soc.*, 1925, **A 108**, 105) suggests that the atoms on the surface of a catalytic material can exist in different degrees of valency saturation. Catalytic action will occur only on those "active" points of the surface where the extent of valency saturation is the least. The number of such active points per unit area of the catalyst surface will obviously depend on the method of preparation of the catalyst. Even if the chemical reaction on which the method of preparation is based remain the same, the number of active points developed per unit area may change considerably due to slight differences in the technique of manipulation. Thus in our experiments catalyst Nos. 1 and 2 had almost the same efficiency (velocity constants for dehydrogenation of pure methyl alcohol being 0·0267 and 0·0253 respectively), while catalyst No. 3 had a much higher efficiency (velocity constant for dehydrogenation being 0·0598). On the basis of Taylor's hypothesis, the number of active points per unit surface of catalyst No. 3 is 2·2 times that on surface of catalyst No. 1 or 2.

It has been observed before that chloroform and carbon disulphide in very small doses enchance the velocity of dehydrogenation of methyl alcohol at the beginning, but diminish very considerably from the beginning the velocity of decomposition of formaldehyde. The poisonous action of mercuric iodide is otherwise. In very small doses, it diminishes very considerably the velocity of dehydrogenation of methyl alcohol but the velocity of decomposition of formaldehyde is only slightly affected. It is clear therefore that these two reactions occur at different points of the catalyst surface, having different chemical and adsorptive properties. It is difficult to explain the accelerating effect of poisons like carbon disulphide and chloroform in very small doses on the velocity of dehydrogenation. It has a curious resemblance to the stimulating action of poisons in very small doses on living organisms.

A remarkable fact is easily noticed in the action of the poisons, carbon disulphide, chloroform and bromine in fairly large doses. *The diminution in the number of active points per unit area and hence the diminution in the velocity constants of dehydrogenation is proportional to the amount of poison added.* Thus we find, that for complete poisoning, 0·0329 gm. of carbon disulphide for 8 gm. of catalyst is required. In Table IV, we find that the velocity constant drops from 0·027 to 0·009 for an addition of 0·023 gm. of carbon disulphide.

We find $\frac{0{\cdot}027-0{\cdot}009}{0{\cdot}027}$ or 0·66 is approximately equal to

$$\frac{0{\cdot}023}{0{\cdot}0329} \text{ or } 0{\cdot}7.$$

Again in the case of chloroform, complete poisoning is effected by the addition of 0·0326 gm., while from Table VII we find that the velocity constant drops from 0·0253 to 0·0053 by an addition of 0·022 gm. of chloroform.

$$\text{We find that } \frac{0{\cdot}0253-0{\cdot}0053}{0{\cdot}025} = 0{\cdot}8,$$

$$\text{and } \frac{0{\cdot}022}{0{\cdot}0326} = 0{\cdot}7 \text{ approximately.}$$

Considering the nature of experimental difficulties in determining the exact amount of poison necessary to inactivate completely the catalyst, the above values may be considered to be almost equal.

In the case of bromine, for complete poisoning 0·168 gm. is required, while to bring the velocity constant down from 0·06 to 0·02, 0·1 gm. of the poison is required (Table X).

$$\text{Here too, } \frac{0{\cdot}06-0{\cdot}02}{0{\cdot}06} = 0{\cdot}66, \quad \text{and } \frac{0{\cdot}1}{0{\cdot}168} = 0{\cdot}6.$$

The ratios are approximately equal.

The experimental data on the amount of various poisons required to stop the reaction completely are given in Table XIV.

TABLE XIV.

Poisons.	Value of K_1 for each catalyst with pure methyl alcohol.	Total amount of poisonous substance required in gm.	Total amount of poisonous element required in gm. atoms of S, Cl, Br, and Hg.	Amount of poisonous element in gm. atom required for completely poisoning 1 gm. atom of the catalyst.	Amount of catalyst used in gm. atom.
1. CS_2	0·0267	0·0329	0·000864	0·00687	0·12568
2. CS_2	0·0267	0·0695	0·00182	0·00724	0·25136
3. $CHCl_3$	0·0252	0·0326	0·000819	0·00651	0·12568
4. Br_2	0·0598	0·01677	0·002009	0·01598	0·12568
5. HgI_2	0·0598	0·01246	0·0000274	0·000218	0·12568

It will be seen from horizontal columns (1) and (2) that with carbon disulphide as poison, as the quantity of catalyst is doubled, the quantity of the poison required for complete poisoning is doubled. From the horizontal columns (1), (2) and (3) it is evident that when a catalyst of the same efficiency is used, the ratio of the gram-atom of sulphur or chlorine to the gram-atom of the catalyst necessary for complete poisoning is approximately the same. Again from the horizontal column (4) we find that with bromine as poison, and with a catalyst whose efficiency is approximately $\frac{0{\cdot}0598}{0{\cdot}0267}$ or 2·2 times that of catalyst in column (1) or (2), the above ratio increases by about 2·2 times. We thus arrive at the remarkable conclusion that *an atom of bromine, an atom of sulphur* (*as* CS_2) *and an atom of chlorine* (*as* $CHCl_3$) *exhibit identical inhibiting power on the dehydrogenation of methyl alcohol by a copper catalyst.*

The behaviour of mercury as poison is fundamentally different. A very much smaller quantity of mercury is sufficient for complete poisoning. It is very probable that here the probable cause of inhibition is to be found in the destruction of the inhomogeneity of the catalytic copper surface due to mercury vapour. In the presence of mercury vapour, the copper surface with its active points where metal atoms are in a condition approximating to that of the gaseous phase, is quickly transformed into a perfect plane crystal face, by mercury vapour condensing on an active point, dissolving it and spreading it out in a smooth layer. The mercury now re-evaporates, condenses on another active point and this reaction is repeated in quick succession.

The experimental data, obtained with carbon tetrachloride or acetonitrile as poisons, do not lend themselves to serious theoretical considerations, as in these cases, the full effect of poison is not perceived immediately on the addition of the poison.

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Use of Phenolic Acids in the Detection, Separation and Estimation of Metals. Part II. Colorimetric Detection and Estimation of Uranium.

By Pabitra Nath Das-Gupta.

At present of all the existing methods* for the detection and estimation of minute quantities of uranium, the sodium salicylate method of Müller stands superior to every other method regarding its sensitiveness. It has however been found that the addition of tannic and gallic acids followed by sodium acetate produced remarkable coloration in uranium solution, which is more sensitive than the sodium salicylate test. As a solution of pyrogallic acid with sodium acetate, on standing, acquires a brown coloration, the detection and estimation were not possible with it; on the other hand, tannic acid with an excess of sodium acetate produces a gelatinous precipitate and hence the colorimetric estimation of uranium by means of tannic acid could not be carried on using excess of sodium acetate.

The phenolic acids, such as tannic, gallic and resorcylic, with dilute uranium solution only produced slight brownish coloration; to these on the addition of sodium acetate the color greatly intensified and became brown. The color produced in each case was not of the same intensity but in the increasing order: tannic, gallic, resorcylic.

In concentrated uranium salt solutions tannic acid produced a red-brown coloration and a partial chocolate brown precipitate. By the addition of sodium acetate to its filtrate, the color was intensified; with an excess of sodium acetate the whole of the uranium

* Colorimetric detection of uranium in minerals by potassium ferrocyanide—Bruttini, *Gazzetta*, 1893, (i) **23**, 253.

Detection of minute quantities of uranium by hydrogen peroxide—Fairly, *Chem. News*, 1890, **62**, 227 (0·5—0·25 mg. detectable).

Detection of uranium by ethylenediamine—Siemssen, *Chem. Zeit.*, 1911, **35**, 139 (sensitiveness as that of hydrogen peroxide and potassium ferrocyanide methods).

Qualitative test of uranium by zinc in presence of nitric acid—Buell, *J. Ind. Eng. Chem.*, 1922, **14**, 593 (0·88 mg. per c c. detectable).

Detection and estimation by sodium salicylate—Müller, *Chem. Zeit.*, 1919 **43**, 739 (0·2 per cent. of the metal estimable).

was precipitated and the filtrate was found to be colorless. Gallic and resorcylic acids in concentrated uranium solutions produced red-brown and brown colorations respectively but no precipitate. An addition of sodium acetate in excess to the mixtures increased the colorations; when however it was left for 2-3 hours, the formation of a gelatinous brown precipitate was observed in the case of gallic acid only. With a very concentrated uranium solution, gallic acid produced red-brown coloration and a precipitate.

The color reaction is more sensitive in uranium salt solution if sodium acetate is added after the addition of phenolic acids, but if the order of addition of these reagents be reversed, the color development is far less intense. It was also observed that the intensity of the color produced was proportional to the amount of uranium present in the solution, the color disappearing on adding dilute mineral acids and acetic acid.

The effect of salts as ammonium chloride, sodium phosphate, potassium pyrosulphate, Rochelle's salt and ammonium fluoride, which are likely to be present in the uranium solution in analyses, was studied. It was found that only in presence of ammonium chloride, the detection (but not the estimation) was possible by means of the phenolic acids.

It is thus evident that the colorimetric estimation of uranium is suitable purely in its neutral solution by tannic, gallic or resorcylic acid and sodium acetate. When uranium is present in acetic, hydrochloric or nitric acid solution, the estimation may be carried out by driving off the acid, or by neutralising the acid solution with caustic soda or better with ammonia. According to Müller, neutral alkali salts do not interfere in the estimation of uranium by sodium salicylate but it was found that potassium chloride imparted a greenish tinge to the original reddish-yellow color and increased its intensity. Hence the estimation in presence of a neutral alkali salt is rather faulty. It was also found that with the increasing amount of sodium salicylate a gradual greenish tinge developed in the solution with increasing intensity. Comparing Müller's with the author's method of estimation, the respective sensitiveness stands in the order: Tannic acid>gallic acid>sodium salicylate>resorcylic acid. It was found that with 0·2 c.c. of 1 per cent. tannic acid and 3 c.c. of 5 per cent. sodium acetate, 0·0115 gm. of uranium per litre could be detected and 0·023 gm. per litre could be accurately estimated. With 2 c.c. of about 1 per cent. gallic acid and 1 c.c. of 5 per cent.

sodium acetate, the detectable amount of uranium is 0·0233 gm. per litre and its estimable amount is 0·0345 g. per litre, whereas with resorcylic acid, the detectable lower limit is 0·069 gm. and with 8 per cent. sodium salicylate, the detectable amount and the estimable amounts are 0·046 gm. per litre.

In estimating uranium, fresh solutions of the acids were always used. The reagents were added in the standard and in the unknown solutions simultaneously and the colorations were immediately compared, as, on standing for a long time, the coloration is affected by the air. In actual estimation it was found that when the volumes of the uranium solution for comparison were not widely different, then using 2 c.c. of 1 per cent. tannic acid and 1 c.c. of 5 per cent. sodium acetate, satisfactory results were obtained. But with widely varying volumes of uranium solutions considerable discrepencies in the results were noticed; the solution containing greater amount of uranium showed less color intensity. By trial, it was found that in every condition, best results were obtained by using 3 c.c. of 5 per cent. sodium acetate instead of 1 c.c. This may be due to the fact that using 3 c.c. of 5 per cent. sodium acetate with 2 c.c. of 1 per cent. tannic acid, the mixture comes to a neutral range, and hence the maximum color production. With the idea of verifying this by p_H measurements, it was found that the p_H of 2 c.c. of 1 per cent. tannic acid made up to 10 c.c. with conductivity water was 3−3·5; that of 2 c.c. of 5 per cent. sodium acetate was 8·7−8·9; and of the uranium nitrate solution (1 c.c. = 0·00023 g. per litre) was 4·3. The p_H of uranium nitrate and tannic acid (1 to 8 c.c. of uranium solutions and 2 c.c. of 1 per cent. tannic acid made up to 10 c.c.) was 2·8−3.

Now the cause of maximum color-effect could have been easily ascertained, if the p_H change in the mixture of uranium solution and tannic acid by the gradual addition of 5 per cent. sodium acetate, could be measured; but as a coloration was produced by the addition of sodium acetate, the measurement was not possible by using indicators. However by taking small volumes of uranium solution (0·5−1 c.c.) and adding to this 2 c.c. of 1 per cent. tannic acid followed by 5 per cent. sodium acetate (1−5 c.c.) it was found that with 3 c.c. of sodium acetate solution the p_H in every case was 6·0 to 6·05.

The color-effect was also studied by keeping the proportions of uranium nitrate, tannic acid and sodium acetate constant and

changing the p_H by Buffer's solutions and the maximum color-effect was produced at p_H 6·1.

It is seen that in p_H 6·1 maximum color-effect is produced and excess of tannic acid or sodium acetate can produce no more color-effect; but with excess of sodium acetate after 8 to 10 minutes the mixtures becomes colloidal. From the behaviour of excess of sodium acetate it can also be said that the cause of maximum color formation is purely a case of colloid formation. Tannic acid with uranium solution forms some sort of compound which remains in solution in colloidal and dissociated state, and the solution is feebly acidic. Sodium acetate neutralises the acid and helps the association and then coagulation. The amount of sodium acetate causing the maximum association of uranium with tannic acid, being capable of remaining in solution, evidently gives maximum color effect and is the important factor in the estimation. In the estimations with gallic acid or resorcylic acid no such difficulties, as in the case of tannic acid, are encountered. In all the cases the comparison of colors is made under similar conditions. The estimations with gallic acid gave most satisfactory results. The estimation with resorcylic acid and also its sensitiveness in comparison with those of tannic and gallic acids are not at all satisfactory. The comparison of colors in the estimations was made in a dipping colorimeter. Comparison in Nessler's tubes also gives good results.

When uranium solution is treated with an excess of tannic acid and an excess of sodium acetate, or with excess of tannic acid ammonium acetate and a drop of dilute ammonia, a quantitative precipitation of uranium is obtained, which on ignition gives U_3O_8. This observation leads to gravimetric method for the estimation of uranium (*vide* Part III).

Experimental.

About 5 g. of uranyl nitrate were dissolved in 250 c.c. of water, and in 25 c.c. of it, uranium was estimated as U_3O_8 by freshly prepared ammonia. Thus the solution contained 0·23 gm. of uranium per 25 c.c. 25 C.c. of this solution were diluted to 100 c.c. and in this solution uranium was estimated colorimetrically by the phenolic acids.

Tannic Acid and Sodium Acetate.

Qualitative Lower Limit.—0·1, 0·2, 0·3, 0·4 and 0·5 c.c. of the dilute uranium solution were taken in five test tubes and water was

added to each, such that with 2 c.c. of 1 per cent. tannic acid (freshly prepared) and 1 c.c. of 5 per cent. sodium acetate the volume was 10 c.c. in each case. To a 6th one 7 c.c. of water were taken and tannic acid and sodium acetate were added as before. Then the effect in each of the five test tubes was compared with that of the 6th one.

No.	Observation.	Remarks.
1st.	Light-brown color.ion noticeable at the meniscus.	The color production nearly the same
2nd.	,, ,,	,,
3rd.	,, ,,	Color production more intense than in the 1st or 2nd.
4th.	Color production in the body of the solution, but more pronounced at the meniscus.	Very faint.
5th.	,, ,,	Fairly perceptible and more intense than in the 4th.
6th.	Colorless solution, extremely faint, yellowish coloration at meniscus.	

Hence the lowest amount of uranium that can be detected by tannic acid and sodium acetate is $0{\cdot}000023 \times 5 = 0{\cdot}000115$ g. in 10 c.c. *i.e.*, 0·0115 g. per litre.

By using 2 c.c. of 1 per cent. tannic acid and 3 c.c. of 5 per cent. sodium acetate (the proportion for ideal condition) the same observations were noticed.

Quantitative Estimation.—As even 2 per cent. solution of tannic acid is brownish in color and strong solutions of tannic acid are more acted on by the air producing deep brown solutions, so, for the estimation, 1 per cent. solution, which has a slight brownish tinge, is perfectly suitable. It has been found that 2 c.c. of this 1 per cent. solution diluted to 10 c.c. with water show no brownish tinge. Hence in the estimations always 2 c.c. of 1 per cent. tannic acid solution are used. Fairly strong solutions of sodium acetate produce a while turbidity or a gelatinous precipitate with tannic acid, hence a weak solution (5 per cent.) is used, which is found to be satisfactory.

In two comparison tubes of a dipping colorimeter, measured volumes of dilute uranium solution were taken and water was added, such that with 2 c.c. of the tannic acid and 1 c.c. of the sodium-

acetate solution, the volume was 10 c.c. in each case. Now by fixing one of the tube at a definite scale reading and sliding the other up and down, the color intensity of the one was matched with the other. The readings are tabulated below:—

Experiment 1.

Tube R—2 c.c. uranium solution.
,, L—3 c.c. ,, ,,

Readings	R ..30	30	30	20	20	10	10	10	
	L...21	20·8	21	14·1	14·0	7	7	7	
Remarks	f...Yellow.			Yellowish.			Almost white.		
	r...19·5-22·5			13-15·2			6·4-7·6		
Readings	R...5	5	5	7·4	7·3	14·1	14·1		
	L...3·5	3·4	3·4	5	5	10	10		
Remarks	f...White.			White.			Yellowish.		
	r...2·7-4·0			6·4-7·8			13·0.15·0		

R—Right hand side tube and
L—Left hand side tube of the calorimeter.
f—Color of the match-field.
r—The range within which the intensity of the color in the two fields begins to appear almost the same, *i.e.*, within which the match point lies.

Experiment 2.

Tube R—3 c.c. uranium solution.
,, L—4 c.c. ,, ,,

Readings	R...30	30	30	20	20	10	10	10	10
	L...22·2	22·7	22·5	14·5	15	7·6	7·8	7·7	7·5
Remarks	f...Yellow.		Yellowish.			Almost white.			
	r...20·8-23·6		13·4-15·7			7·0-8·0			

Experiment 3.

Tube R—6 c.c. uranium solution.
,, L—7 c.c. ,, ,,

Readings	R...10	10	5	5	5	6	5·8	5·9
	L...8·7	8·3	4·1	4·3	4·2	5	5	5
Remarks	f...Slight yellowish.		Almost white.			Almost white.		

From the experiments it is seen that good results are obtained when the match field is almost white; as this enables one to detect a sharp change in the field of comparison.

Experiment 4.

Tube R—2 c.c. uranium solution.
,, L—6 c.c. ,, ,,

Readings	R...30	30	20	20	10	10	
	L...11·7	11·5	7·7	7·7	3·8	3·8	
Remarks	f...Yellow.		Yellowish.			Almost white.	
	r ..11-12·2		7·0-8·1			3·2-4·2	

Experiment 5.

Tube R—1 c.c. uranium solution.
,, L—3 c.c. ,, ,,

Readings	R...30	30	20	20	20	10	10
	L...11·8	11·7	7·6	7·7	7·9	3·6	3·7
Remarks	f...Light yellow.		Almost white.			White.	
	r...10·5-12·6		6·7-8·6			2·7-4·4	

Experiment 6.

Tube R—2 c.c. uranium solution.
,, L—7 c.c. ,, ,,

Readings	R...25	25	20	20	15	15	10	10
	L ..10·7	10·7	8·7	8·7	6·5	6·6	4·5	4·4
Remarks	f...Yellowish.		Yellowish tinge.		Almost white.		White.	
	r...10·0-12·0		8·0-10·0		6·0-7·5		3·7-4·7	

From the readings of the Expts. 4, 5 and 6 it is seen that L's with comparatively higher amounts of uranium than the R's show weaker color-effect than that expected. As the match point is very sharp, *i.e.*, within 1—1·2 scale reading and it is likely that with so much uranium the color is not fully developed, so to get maximum color development either more tannic acid solution or more sodium acetate requires to be added. Whereas in Experiments 1, 2 and 3 with closer amounts of uranium the color-effects in two cases cannot materially effect the estimation. By numerous trials the

ideal conditions, which give good results, are to use 2 c.c. of 1% tannic acid and 3 c.c. of 5% sodium acetate solution and the results thereof are given below. In these cases also the volumes of the solution for comparision are 10 c.c.

Experiment 7.

Tube R—3 c.c. uranium solution.
,, L—5 c.c. ,, ,,

Readings	R...30	30	25	25	20	20	15	15	10	10
	L...18	18	14·8	14·9	11·9	11·9	8·8	8·9	5·8	6·0
Remarks	f...Deep yellow.		Yellow.		Yellow.		Light yellow.		Yellowish.	
	r...17·2-18·8		14·2-15·8		11·4-12·6		8·3-9·6		5·6-6·4	

Experiment 8.

Tube R—1 c.c. uranium solution.
,, L—3 c.c. ,, ,,

Readings	R...30	30	25	25	20	20	15	15	10	10
	L...10·8	10·8	9	8·9	7·4	7·3	5·5	5·5	3·3	3·4
Remarks	f...Light yellow.		Yellowish.		Almost white.		White.		White.	
	r...10·2-11·3		8·6-9·7		6·7-7·8		5·0-6·0		2·9-3·9	

Experiment 9.

Tube R—2 c.c. uranium solution.
,, L—3 c.c. ,, ,,

Readings	R...30	30	25	25	20	20	15	15	10	10
	L...20·4	20·5	17·3	17·3	13·6	13·5	10·3	10·2	6·7	6·7
Remarks	f...Yellow.		Yellow.		Yellowish.		Yellowish.		Almost white.	
	r...19·4-21·5		16·6-18·8		12·7-14·4		9·7-10·9		6·2-7·3	

In all the experiments it is seen that when the match field is white or almost white, the range is small and the results of comparison are more accurate. So, for comparison, always white or almost white field should be brought about.

Maximum Color Development under the Ideal Condition.—The probable causes of the maximum color production have been discussed before. However, in support of the cause due to p_H, another

point is noticed as follows: studying the p_H values of uranium solution and sodium acetate it is observed that 1 c.c. uranium solution + 1 c.c. sodium acetate made up to 10 c.c. with water give p_H 6·9 and 3 c.c. uranium solution + 3 c.c. sodium acetate made up to the same volume give p_H 6·9; so it is expected that with 2 c.c. tannic acid in each case there should be produced a color-effect in the ratio of 1 : 3, and actually this is the case.

Experiment 10.

	U soln.			Sodium acetate.				Water.		Tannic acid.	
	R—1 c.c.			1 c. c.				6 c.c.		2 c.c.	
	L—3 c.c.			3 c.c.				2 c.c.		2 c.c.	
Readings	R...30	30	30	25	25	20	20	15	15	10	10
	L...10·3	10·1	10	8·7	8·5	6·9	7·0	5·1	5·2	3·4	3·5
Remarks	*f*...Yellowish.			Yellowish tinge.		Almost white.		Almost white.		White.	
	r...9·6-11·0			8·0-9·3		6·6-7·6		4·7-5·7		3·0-4·0	

Experiment 11.

Tube R—0·5 c.c. uranium solution.
,, L—1·0 c.c. ,, ,,

Readings	R...30	25	25	20	20	15	15	10
	L...16·9	14·1	14·4	11·8	11·5	8·7	8·9	5·6

Experiment 12.

Tube R—0·5 c.c. uranium solution.
,, L—0·6 c.c. ,, ,,

Readings	R...30	30	25	25	20	20	15	10	10
	L...25·4	25·0	21·2	21·3	17·0	17·3	12·4	8·4	8·5
	r...24·3-27·3		19·0-22·0		15·8-18·6		11·0-13·7		7·4-10·0

Experiment 13.

Tube R—1·0 c.c. uranium solution.
,, L—1·5 c.c. ,, ,,

Readings	R...30	30	25	25	20	20	15	15	10	10
	L...20·2	20·5	17	17	13·4	13·6	10·2	10·2	7·0	6·9
	r...19-21		16·4-18		12·8-14·6					

From the above experiments it is seen that with 1 c.c. of the uranium solution (0·00023 g. U) the estimation is most satisfactory. In Expt. 12, however, good results are obtained, but the range is greater. So 0·00023 g. of uranium in 10 c.c., *i.e.*, 0·023 g. per litre can be very well estimated.

Determination in Nessler's Colorimeter.

Tannic acid solution = 2 c.c.
Sodium acetate ,, = 3 c.c.

Expts.	Tubes.	U-soln. taken (c.c.)	Match point. Water added. (c.c.)	Match point. Total vol. (c.c.)	Found. (c.c.)	Taken.
14	A	x	y	50	4·08	4·0 c.c
	B	4	40	49		
15	A	x	y	50	3·4	3·5
	B	1·5	16·5	22		
16	A	x	y	50	2·94	3·0
	B	2	27	34		
17	A	x	y	100	5·26	5·5
	B	1	13	19		

Estimation in Presence of Acids.—To uranium solution, nitric or hydrochloric acid is added, the acid is driven off by repeated evaporation with little water. The residue is then taken up with water in a Nessler's tube (A); 2 c.c. tannic acid and 3 c.c. sodium acetate solutions are added, the volume is made up to 50 c.c. with water; the color in the tube thus produced is matched with the color by adding measured volumes of water in the other tube (B), where a known amount of uranium is present.

Expts.	Tubes.	U soln. taken. (c.c.)	Vols. at match-point (c.c.)	Found (c.c.).
18	A	2	50	1·97
	B	1·5	38	
19	A	3	50	2·94
	B	1	17	
20	A	3	50	3·03
	B	2	33	
21	A	4	50	4·17
	B	5	60	

Detection and Estimation by Means of Gallic Acid and Sodium Acetate.—In this case the limit is determined just as in the case of tannic acid using 2 c.c. 1% gallic acid and 1 c.c. 5% sodium acetate solutions and is found to be 0·023 g. per litre. But addition of ammonium chloride increases the sensitiveness.

Quantitative Estimation.—Under the following experimental conditions, as tabulated, readings are taken and are given below.

Expts.	Tubes.	U soln. (c.c.)	1 % Gallic acid (c.c.)	5% Sodium acetate. (c.c.)	Water. (c.c.)	Total vol. (c.c.)
22	R	2	2	4	2	10
	L	4	.	.	—	,,
23	R	2	4	2	2	10
	L	4	4	2	—	,,
24	R	2	2	1	5	,,
	L	6	,,	,,	1	,,
25	R	2·0	1·5	2	4·5	,,
	L	6	,,	,,	0·5	,,
26	R	1·5	2	2·0	4·5	,,
	L	8	2	—	—	,,

Corresponding readings:—

Expt. 22	R...30	30	20	20	10	10			
	L...15·8	15·4	10·3	19·2	5·2	5·1			
Expt. 23	R...30	30	20	20	10	10			
	L...15·8	15·4	10·3	10·2	5·2	5·1			
Expt. 24	R...30	30	25	25	20	20	15	15	
	L...9·9	9·9	8·3	8·4	6·7	6·8	4·8	5·0	
Expt. 25	R...30	30	25	25	20	20	15	15	
	L...10·0	9·9	8·2	8·4	9·7	6·6	5·0	5·0	
Expt. 26	R...30	30	25	25	20	20			
	L...7·4	7·5	6·5	6·5	5·1	5·1			

In all these experiments the range is within one division of scale reading.

Estimation in Presence of Ammonium Chloride.

Fxpts.	Tubes.	U soln. (c.c.)	NH_4Cl soln. (c.c.)	1% Gallic acid. (c.c.)	5% Sodium acetate. (c.c.)	Water. (c.c.)	Total vol. (c.c.)
27	R...	2	2	2	2	4	12
	L...	6	,,	,,	,,	—	,,
28	R...	2	2	2	2	2	10
	L...	6	—	2	2	—	,,

Corresponding readings:—

Expt. 27	R...	30	30	25	25	20	20	15	15	10	10
	L...	10·2	10·1	8·7	8·5	6·8	6·8	5·0	5·1	3·5	3·3
Expt. 28	R...	30	30	20	20	10	10				
	L...	12·5	12·5	8·5	8·5	4·3	4·2				

From the readings of Expts. 27 and 28 it is clear that with ammonium chloride the color-effect is much increased than in the case where no ammonium chloride is used. But by adding the same amount of ammonium chloride the estimation is all right, as seen in Expt. 27. So in the presence of ammonium chloride (unknown amount) the estimation is not suitable. The only advantage of ammonium chloride is that it increases the sensitiveness.

Detection and Estimation with Resorcylic Acid and Sodium Acetate.—A faint yellow coloration is noticed in the body of 10 c.c. solution using 3 c.c. of the dilute uranium solution, *i.e.*, 0·069 g. of uranium per litre is detectable. Under similar conditions (that is with 2 c.c. resorcylic acid and 1 c.c. sodium acetate, the total volme being 10 c.c.) to the following experiments are done. This shows that the estimation with resorcylic acid is not at all satisfactory for reasons of low sensitiveness and high range.

Expt.	Tubes.	U soln. (c.c.)		
29	R...	3	Readings	R...30 30 20 20
	L...	4		L...21 21 14·6 15·6
				r... 19-23 14-18
30	R...	5	Readings	R...25 25 20 20
	L...	4		L...29 29·2 23 22·5
				r... 26·5-30 20·6-26
31	R...	5	Readings	R...30 30 30 20 20
	L...	6		L...24·3 24 24·5 16·6 17
				r... 23-26 14·6-17·6

Estimation with Sodium Salicylate: Effect of Neutral alkali Salt.

Expts.	Tubes.	U soln. (c.c.)	Water. (c.c.)	KCl soln.	Na-salicylate soln.	Total vol. (c.c.)
32	R	4	4	—	2 c.c. of 4%	10
	L	,,	—	4 c.c. 20%	,,	,,
33	R	5	3	—	2 c.c. of 8%	,,
	L	,,	—	3 c.c. of 10%	,,	,,

Corresponding readings:—

Expt. 32	R...30	20	20	10		
	L...19	13·6	13	7·1		
Expt. 33	R...30	30	20	20	10	10
	L...26·2	26·7	17·9	18	9·0	9·1
	r...25·2-27·6		17-19·4		8-10	

With potassium chloride the reddish-yellow color produced by sodium salicylate only is changed and a greenish shade is obtained, which causes a difficulty to get the match-point. But by adjusting the field to a white or almost white shade, somewhat accurate match-points were obtained. From Expts. 32 and 33 it is evident that the solution to which potassium chloride is added appears stronger and the more the potassium chloride in the solution, the more the color-effect.

Effect of Excess of Sodium Salicylate.—From several qualitative experiments and the comparison experiment given below it has been found that with excess of sodium salicylate the color with uranium solution intensifies, but a greenish tinge is imparted to the color, which renders the comparison very difficult.

Expt. 34	Tubes.	U soln.	Water.	Na-salicylate.	Total vol.	Remarks.
	R...	5 c.c.	3 c.c.	2 c.c. of 1%	10 c.c.	Reddish-yellow col.
	L...	,,	,,	2 c.c. of 8%	,,	Greenish-yellow col.
Readings	R...	30	20	10		
	L...	No match pt.		5·6 (roughly adjusted)		

As with higher concentrations of sodium salicylate the color-effect is greater, so with 8% solution of sodium salicylate some determinations were carried out. In each case 2 c.c. of 8% sodium salicylate were added and the volume was made up to 10 c.c.

Expts.	Tubes.	U soln.								
35	R...	2 c.c.	Readings	R...	19	10	Remarks	f... White.		
	L...	5 c.c.		L...	3·7	3·8		r... 2·5-4·7		
36	R...	3 c.c.	Readings	R...	30	30	25	25	20	20	10
	L...	5 c.c.		L...	18·3	18·1	14·5	14·7	11·8	11·8	5·6
			Remarks	f...	Yellowish.		Yellowish tinge.		Almost; white.		White.
				r...	17-19		13·7-15·5		10·5-12·2		4-6

After all it is seen that best results are obtained with gallic acid and sodium acetate.

The action of these phenolic acid has also been studied on other metallic salt solutions with sucessful results. Further work on the subject is in progress.

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Use of Phenolic Acids in the Detection, Separation and Estimation of Metals. Part III. Gravimetric Estimation of Uranium.

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In the existing methods of gravimetric estimation of uranium, the latter is precipitated, converted into U_3O_8 or UO_2 and weighed as such. The forms in which uranium is precipitated from its solution (for gravimetric estimation) are $(NH_4)_2U_2O_7$, UF_4 and UO_2S ; all of them on ignition in air are changed into U_3O_8.

It has been observed that from a neutral or faintly acid solution or from a solution containing suspended $(NH_4)_2U_2O_7$ uranium can be quantitatively precipitated by tannic acid followed by the addition of a solution of sodium acetate and some ammonium salts (preferably chloride or nitrate) or of a slightly ammoniacal ammonium acetate solution. This uranium precipitate on ignition in air is changed into U_3O_8. The above observations serve as a gravimetric method for the estimation of uranium, which is dealt with in the present paper.

For the quantitative precipitation of uranium from its solution, the following points are to be observed.

1. When uranium is present as nitrate, chloride or sulphate in neutral or faintly acid solution, addition of some alkali or ammonium acetate is essential. The acetate added should not be less than the amount required to neutralise the mineral acidity which will be liberated in the reaction.

2. Addition of alkali acetate must be followed by an ammonium salt for coagulating the uranium precipitate ; its amount depends on the strength of the uranium solution, with very weak solution greater amount of the salt requires to be added. In the case of the acetate solution, containing no free mineral acids, addition of an acetate is not required.

3. In the presence of free mineral acids or an excess of acetic acid, the acidity is to be neutralised by adding ammonium hydroxide till the solution is just opalescent.

4. If ammonium acetate is used instead of sodium acetate, it should be made faintly ammoniacal.

The precipitate obtained from uranyl nitrate solution by tannic acid and other reagents stated above is found to be free from nitrate and acetate radicles. The uranium precipitate with excess of water forms pseudo-solution, chocolate-brown in colour like that of the precipitate; addition of ammonium salts to this solution gives rise to the original precipitate. The uranium precipitate is found to be very stable. It does not break even on boiling with ammonium or sodium hydroxides, nor does it dissolve in ammonium or sodium carbonate. It is readily soluble in dilute mineral acids and in excess of dilute acetic acid giving colourless solutions.

Experimental.

An aqueous solution of uranyl nitrate is prepared. With this solution, several estimations of uranium are carried out according to the standard method. Uranium is first precipitated as $(NH_4)_2U_2O_7$ by ammonium chloride and freshly prepared ammonia and then ignited to U_3O_8 and weighed. Also side by side from this solution uranium is estimated according to the present method. The results of the above estimations are tabulated below:

Weitght of U_3O_8.

Uranium solution taken (c.c.)	Ammonium hydroxide mothod.	Tannic acid method.	Remarks.
10	0·1434 g.	0·1436 g.	
5	0·0718	0·0722	
,,	0·0710	0 0721	With original uranium solution.
,,	0·0720	0·0719	
3	Estimation not possible.	0·0430	
,,	,,	0·0434	
2	,,	0·0285	
,,	,,	0·0289	
1	,,	0·0144	
,,	,,	0·0148	
20		0·0286 g.	
15		0·0217	The uranium solution is diluted 10 times.
,,		0·0219	
10		0·0144	
,,		0·0144	
5		0·0072	
,,		0·0073	
10	0·1405 g.	0·1402 g.	With fresh uranium solution.
,,	0·1400	—	
5	—	0·0700	

To estimate uranium according to the tannic acid method, the best condition for its precipitation is to add 2 c.c. of 2% tannic acid for each 0·012 g. of uranium. After the addition of tannic acid, which produces a deep brown coloration, the solution is just boiled and to this ammoniacal 10% ammonium acetate solution is added with stirring till the upper liquid becomes clear. For a certain amount of uranium, the quantity of ammonium acetate varies with concentration, *e.g.*, for 0·012 g. uranium in 1 c.c., 0·5 c.c. of ammonium acetate is sufficient for the complete precipitation and for the same amount in a volume of 10 c.c. at least 1·5 c.c. ammonium acetate are required. The precipitate of uranium obtained in this way is chocolate-brown in colour and is very voluminous ; it affords moderately quick filtration. When a solution contains purely uranium salt, the precipitate is filtered and the last traces of the precipitate are taken on the filter by warm and slightly ammoniacal 2% ammonium nitrate solution. The precipitate is then ready for wet incineration. When the precipitate requires decantation washing (say, in the presence of sodium or other salts not precipitable by tannic acid and ammonium acetate), it is done by stirring the precipitate with 100-120 c.c. of warm ammoniacal 2 % ammonium nitrate solution and each time allowed to settle for 10 minutes and then the clear liquid is decanted through the filter.

The advantages of the present method are :—

(1) Accurate results are obtained. (2) With small amount of uranium, the gravimetric estimation is fairly good. (3) There is no possibility of low results, which may occur in the standard method, due to the presence of slight ammonium carbonate in ammonia.

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Basicity and Constitution of Some Inorganic Acids from Electric Conductivity and Coagulation Experiments.

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In a recent paper (Dhar, *J. Indian Chem. Soc.*, 1928, **5**, 585), it has been shown that fluoride and iodate ions behave practically as divalent ions. In this communication we have tried to throw light on the basicity and constitution of some inorganic acids by measurements of the electric conductivity and coagulating powers of their respective sodium or potassium salts.

Hypophosphorous Acid.

Kahlbaum's pure hypophosphorous acid was neutralised with pure caustic soda and a stock solution was obtained. The exact concentration of the sodium hypophosphite solution was determined by oxidizing a known volume of the solution to phosphate by fuming nitric acid and weighing as $Mg_2P_2O_7$.

The following results were obtained in the measurements of equivalent conductivity of a solution of sodium hypophosphite at 30°.

Equivalent conductivity ...	51·4	68·4	82·2	92	100·5	105·6
Concentration ...	*N*/·6815	*N*/1·363	*N*/2·726	*N*/5·462	*N*/10·904	*N*/21·804
Equivalent conductivity ...	110·05	112·6	115·07	116·2	116·7	
Concentration ...	*N*/43·608	*N*/87·216	*N*/174·432	*N*/348·864	*N*/697·7	

From this we find that $\mu 697{\cdot}7 - \mu 21{\cdot}8 = 11{\cdot}1$.
Hence the acid appears to be monobasic.

Coagulation Experiments.

$Fe_2O_3 = 4{\cdot}88$ g. per litre. $ZrO_2 = 10{\cdot}34$ g. per litre.
$CeO_2 = 6{\cdot}16$,, ,, ,, $Cl_2 = 0{\cdot}7506$,, ,, ,,

Sol.	Amt. taken. (c.c.)	Total volume (c.c.)	KCl required for coagulation.	Sodium hypophosphite required for coagulation.	Ratio of KCl to sodium hypophosphite.
$Fe(OH)_3$	1	10	2 c.c. $N/20$	1·2 c.c. $N/68$	5·6
$Ce(OH)_4$	1	5	1·4 c.c. $N/5$	0·4 c.c. $N/20·6$	14·12
$Zr(OH)_4$	1	5	1·3 c.c. $N/5$	0·6 c.c. $N/20·6$	8·9

The experimental results on conductivity measurements with sodium hypophosphite show that $\mu 697·7 - \mu 0·6815 = 65·25$, whilst the difference between equivalent conductivities of potassium chloride and potassium fluoride between $N/1001·4$ and $N/0·9843$ is 42·1 and 41·5 respectively. These results seem to show that hypophosphorous acid has a tendency to be dibasic and this conclusion is supported from the coagulation experiments. The coagulating power of sodium hypophosphite is about eight times greater than that of potassium chloride on $Zr(OH)_4$ sol, fourteen times greater with $Ce(OH)_4$ and six times greater with $Fe(OH)_3$. It should, however, be mentioned here that the coagulating power of caustic soda or potash on these sols is much greater than that of potassium chloride because alkalis react chemically on the peptising electrolytes which lead to the stabilisation of these sols.

Cornec (*Ann. Chim. Phys.*, 1913, *viii*, **29**, 490) measured the lowering of the freezing point of solutions of hypophosphorous acid when progressively neutralised with sodium or ammonium hydroxide. The resulting simple curve is characteristic of monobasic acids. From the heat of neutralisation of hypophosphorous acid by sodium or barium hydroxide Thomsen concluded that it is a monobasic acid.

Our experiments on electric conductivity and coagulation show that the acid is monobasic with a slight tendency to be dibasic.

Phosphorous Acid.

Kahlbaum's pure phosphorous acid was neutralised with pure sodium hydroxide and the exact strength was determined in the same way as hypophosphorous acid.

The following results were obtained with electric conductivity measurements and coagulation with sodium phosphite solutions:—

Concentration.		μ	Concentration.		μ
$N/3·792$	...	110·3	$N/120·544$	...	181·6
$N/7·584$	...	127·7	$N/241·086$	...	189·5
$N/15·068$	...	142	$N/482·176$	.	197·5
$N/30·136$	...	156·4	$N/964·352$	...	201·6
$N/60·272$	...	169·5	$N/1928·704$	...	205·2

Coagulation Experiments.

Fe_2O_3 = 4·88 g. per litre
CeO_2 = 6·16 g. ,, ,,
ZrO_2 = 10·34 g. ,, ,,

Sol.	Amount. (c.c.)	Total volume. (c.c.)	KCl reqd.	Sodium phosphite.	Ratio of KCl to sodium phosphite.
$Fe(OH)_3$	1	5	2 c.c. *N*/20	0·6 c.c. *N*/454	75·6
$Ce(OH)_4$	1	5	1·4 c.c. *N*/0·5	1 c.c. *N*/130	36·4
$Zr(OH)_4$	1	5	1·3 c.c. *N*/5	2 c.c. *N*/130	16·9

Cornec (*ibid*, 1913, *viii*, **30**, 63) measured the lowering of freezing point of solutions of phosphorous acid when progressively neutralised by sodium or ammonium hydroxide and observed two breaks in the curve corresponding with the dibasicity of the acid; this conclusion is in agreement with Thomsen's thermochemical observations.

Italiener ("Beiträge zur Kenntnis der phosphorigen Säure und ihrer Salze," Freiburg i. Br., 1917) has concluded from freezing and boiling points measurements that phosphorous acid is markedly polymerised and exists as $(H_3PO_3)_2$ and the complex molecule is ionised. Thus:— $H_6P_2O_6 \rightleftharpoons H^\circ + H_5P_2O_6'$ and $H_6P_2O_6 \rightleftharpoons 2H^\circ + H_4P_2O_6''$. If we calculate the values of *i* from the freezing-point lowering and boiling-point elevation measurements of Italiener on the basis that phosphorous acid exists as H_3PO_3, the following results are obtained:—

i from F.P. ...	1·34	1·54	1·52	1·66
Concentration ...	1·186	0·539	0·296	0·148
i from B.P. ...	0·93	1·02	1·17	1·9
Concentration ...	0·976	0·488	0·244	0·122

Now if phosphorous acid existed as $H_6P_2O_6$ and it is ionised as $H_6P_2O_6 \rightleftharpoons 2H^\circ + H_4P_2O_6''$, as has been assumed by Italiener, the values of *i* at the concentrations of 0·148 and 0·122 would have been 3·32 (F.P.) and 3·8 (B.P.) respectively. However, according to the assumption of Italiener, the number of ions avilable from the polymerised molecules of phosphorous acid is three and not four, which is approximately the experimental value. Hence, it appears that the conclusion of Italiener is doubtful. Our results on electric

conductivity and coagulation show that phosphorous acid behaves as a dibasic acid with a slight tendency to be tribasic.

Iodic Acid.

Kahlbaum's pure potassium iodate was several times recrystallised from conductivity water and the following results were obtained:—

Dilution ...	32	64	128	256	512	1024
Equivalent conductivity at 21° ...	90·1	93·95	97·29	100·45	103·4	105·95

From these we find that $\mu 1024 - \mu 32 = 15{\cdot}85$, a value which is higher than ten. Hence iodic acid appears to have a marked tendency to be dibasic. It has also been observed that the conductivity of potassium iodate does not become constant even at a dilution of 1024. This is in agreement with our view that iodic acid and iodates exist partly in the polymerised condition. Our results are not in agreement with those of Walden ("Leitvermogen der Lösungen," 1924, Vol. II, p. 113) who obtained the value 11·9 for $\mu 1024 - \mu 32$ with potassium iodate at 25°. The following are the results of the coagulation experiments:—

$CeO_2 = 6{\cdot}16$ g. per litre. $Fe_2O_3 = 11{\cdot}43$g. per litre.

$ZrO_2 = 10{\cdot}34$ g. per litre. $Cl = 0{\cdot}7506$ g. per litre.

Sol.	Amount. (c.c.)	Total volume. (c.c.)	KCl required.	KIO_3 required.	Ratio of KCl to KIO_3.
$Ce(OH)_4$	1	5	1·4 c.c. *N*/5	0·6 c.c. *N*/125	58
$Zr(OH)_4$	1	,,	1·3 ,, *N*/5	1·6 ,, *N*/125	20·3
$Fe(OH)_3$	1	,,	1·5 ,, *N*/5	1·0 ,, *N*/108	35·4

Hence the coagulating power of iodate ion is of the same order as that of a bivalent ion.

Titanic Acid.

Kahlbaum's potassium titanate was washed with alcohol to remove free alkali. The following results were obtained on the coagulation of some hydroxide sol by potassium titanate. In order to get

comparable results, the same sols were coagulated by potassium sulphate under identical conditions:—

ZrO_2 = 10·34 g. per litre. Fe_2O_3 = 11·4 g. per litre.

Sol.	Amount. (c.c.)	Total volume. (c.c.)	KCl required.	Potassium titanate.	Ratio of KCl to potassium titanate.
$Zr(OH)_4$	1	5	1·3 c.c. *N*/5	3·3 c.c. *N*/220	19
$Fe(OH)_3$	1	5	1·5 c.c. *N*/5	2·9 „ *N*/220	22·8

ZrO_2 = 10·34 g. per litre. Fe_2O_3 = 11·4 g. per litre.

Sol.	Amount taken. (c.c.)	Total volume. (c.c.)	KCl required.	K_2SO_4 reqd.	Ratio of KCl to K_2SO_4.
$Zr(CH)_4$	1	5	1·3 c.c. *N*/5	1 c.c. *N*/100	26
$Fe(OH)_3$	1	5	1·5 c.c. *N*/5	0·8 c.c. *N*/100	37·5

Hence titanate ion behaves as bivalent ions towards the coagulation of some hydroxide sols.

Antimonic Acid.

The following results were obtained in the coagulation of some hydroxide sols by $K_2H_2Sb_2O_7$.

CeO_2 = 6·16 g. per litre.

ZrO_2 = 10·34 g. „ „

Fe_2O_3 = 11·45 g. „ „

Sol.	Amount taken. (c.c.)	Total volume. (c.c.)	KCl required.	Potassium antimonate required.	Ratio of KCl to potassium antimonate.
$Ce(OH)_4$	1	5	1·4 c.c. *N*/5	1·5 c.c. *N*/200	37·3
$Zr(OH)_4$	1	5	1·3 c.c. *N*/5	3·2 c.c. *N*/200	16·2
$Fe(OH)_3$	1	5	1·50 c.c *N*/5	0·8 c.c. *N*/100	37·5

The coagulation experiments are in favour of the view that potassium pyroantimonate gives out a bivalent ion in solution. The electric conductivity measurements of Tornula (*Z. anorg. Chem.*, 1921, **118**, 84) with potassium antimonate show a slight decrease of conductivity on dilution. Similar results were obtained with sodium vanadate,

Boric Acid.

The following results were obtained on the electric conductivity measurements with solutions of pure borax at 21°.

Dilution ...	8	16	32	64	128	256	512	1024
Equivalent conductivity ...	55·3	61·1	66·5	70·8	74·9	77·5	80	82

Hence $\mu 1024 - \mu 32 = 15{\cdot}5$. The same value ($\mu 1024 - \mu 32 = 15{\cdot}5$) was obtained by Rosenheim (*Z. anorg. Chem.*, 1921, **119**, 26) with $K_2B_4O_7$ solutions at 0°.

The results of the coagulation experiments are as follows:—

$ZrO_2 = 10{\cdot}34$ g. per litre.

$Fe_2O_3 = 11{\cdot}43$ g. per litre.

Sol.	Amount taken. (c.c.)	Total volume (c.c.)	KCl required.	Borax required.	Ratio of KCl to borax.
$Zr(OH)_4$	1	5	1·3 c.c. *N*/5	1·2 c.c. *N*/125	27
$Fe(OH)_3$	1	5	1·5 c.c. *N*/5	1·0 c.c. *N*/125	37·5

It appears, therefore, that the negative ions given out from a solution of borax are bivalent.

Vanadic Acid.

The following results were obtained in the measurement of electric conductivity of sodium vanadate solutions at 21°.

Dilution ...	19	38	76	152	304
Equivalent conductivity ...	117·8	122·4	127	125·4	113·2

Düllberg (*Z. physikal. Chem.*, 1903, **45**, 129) obtained similar decrease of conductivity on dilution with a solution of $(NaVO_3)_3$.

The following are the results of coagulation experiments:—

$CeO_2 = 6{\cdot}16$ g. per litre.

$ZrO_2 = 10{\cdot}34$ g. ,, ,,

$Fe_2O_3 = 11{\cdot}43$ g. ,, ,,

Sol.	Amount taken. (c.c.)	Total volume. (c.c.)	KCl required.	Sodium vanadate required.	Ratio of KCl to sodium vanadate.
$Ce(OH)_4$	1	5	1·4 c.c. *N*/5	2·2 c.c. *N*/380	48·3
$Zr(OH)_4$	1	5	1·3 c.c. *N*/5	3·9 c.c. *N*/880	25·3
$Fe(OH)_3$	1	5	1·5 c.c. *N*/5	1·1 c.c *N*/160	43·7

The coagulation results show that vanadate ion is bivalent.

Tungstic Acid.

The conductivity results with solutions of sodium tungstate at 21° are as follows:—

Dilution ...	8	16	32	64	128	256	512	1024
Equivalent conductivity ...	77·6	82·9	87·3	91·3	95·3	99·1	101·3	103·9

Hence $\mu 1024 - \mu 32 = 16{\cdot}6$ with sodium tungstate solution. Walden (*ibid*, p. 117) found for $\mu 1024 - \mu 32$ the value 21·5 with a solution of normal sodium tungstate.

The following results were obtained in the coagulation of some hydroxides with sodium tungstate.

$CeO_2 = 6{\cdot}14$ g. per litre.
$ZrO_2 = 10{\cdot}34$ g. ,, ,,
$Fe_2O_3 = 11{\cdot}33$ g. ,, ,,

Sol.	Amount taken (c.c.).	Total volume (c.c.).	KCl required.	Na_2WO_4 required.	Ratio of KCl to Na_2WO_4.
$Ce(OH)_4$	1	5	1·4 c.c. *N*/150	0·9 c.c. *N*/5	46·6
$Zr(OH)_4$	1	5	1·3 c.c. *N*/5	1·8 c.c. *N*/150	2·2
$Fe(OH)_3$	1	5	1·5 c.c. *N*/5	0·8 c.c. *N*/125	47

Hence tungstate ion appears to be bivalent and tungstic acid is dibasic.

Molybdic Acid.

The following results have been obtained with potassium molybdate and ammonium molybdate solutions regarding electric conductivity at 21°.

Potassium molybdate.

Dilution. ..	32	64	128	256	512	1024
Equivalent conductivity. ...	108·5	113·7	119·8	125	128·8	132·5

Ammonium molybdate.

Dilution. ...	16	32	64	128	256	512	1024
Equivalent conductivity. ...	84·5	96·45	108·8	120·3	128·6	136·9	143·5

Hence $\mu 1024 - \mu 32$ for potassium molybdate = 24 and = 47·05 for ammonium molybdate.

Grossmann (*Z. anorg. Chem.*, 1904, **41**, 47) obtained the value 22·4 for $\mu 1024 - \mu 32$ with a solution of sodium molybdate at 25°.

The coagulation experiments are as follows:—

CeO_2 = 6·16 g. per litre. Fe_2O_3 = 11·43 g. per litre.
ZrO_2 = 10·36 g. ,, ,,

Sol.	Amount taken (c.c.).	Total volume (c.c.).	KCl required.	K-molybdate.	Ratio of KCl to K-molybdate.
$Ce(OH)_4$	1	5	1·4 c.c. *N*/5	0·9 c.c. *N*/150	46·6
$Zr(OH)_4$	1	5	1·3 c.c. *N*/5	1·8 c.c. *N*/150	22
$Fe(OH)_3$	1	5	1·5 c.c. *N*/5	0·9 c.c. *N*/125	41·6

CeO_2 = 6·16 g. per litre. Fe_2O_3 = 11·43 g. per litre.
ZrO_2 = 10·36 g. ,, ,,

Sol.	Amount taken (c.c.).	Total volume (c.c.)	KCl required.	Ammonium molybdate.	Ratio of KCl to ammonium molybdate.
$Ce(OH)_4$	1	5	1·4 c.c. *N*/5	1·9 c.c. *N*/400	59
$Zr(OH)_4$	1	5	1·3 c.c. *N*/5	3·7 c.c. *N*/400	28·1

We have carefully compared the electric conductivities of potassium chloride and fluoride under identical condition and the results are as follows:—

Concentration.	μ of KF.	μ of KCl	Concentration.	μ of KF.	μ of KCl.
N/0·9843 ...	92·5	114·5	*N*/62·539 ...	131·2	152·3
N/1·9886 ...	102·3	122·5	*N*/125·068 ...	132·7	154·3
N/3·976 ...	111·68	130·5	*N*/250·13 ...	133·5	155·6
N/7·842 ...	118·7	138·8	*N*/500·27 ...	133·8	156·4
N/15·63 ...	124·1	143·9	*N*/1001·44 ...	134	156·6
N/31·259 ...	128	148	*N*/2002·88 ...	*x*	*x*

The conductivity measurements do not support the dibasic nature of hydrofluoric acid, although the coagulation experiments of Ghosh and Dhar (*Kolloid Z.*, 1928, **44**, 149; *J. Indian Chem. Soc.*, 1928, **5**, 303) with several sols are in favour of the bivalent nature of fluoride ion.

In previous papers (*Z. anorg. Chem.*, 1922, **121**, 99 ; *J. Indian Chem., Soc.*, 1928, **5**, 585) evidence has been brought forward in favour of the view that chromic acid in solution exists mainly as H_2CrO_4 and potassium dichromate exists in solution chiefly as $KHCrO_4$. Evidently the coagulating power of potassium chromate should be greater than that of potassium dichromate, because the number of bivalent CrO_4'' ions will be greater in chromate solutions than in dichromate solutions of equivalent concentration. This conclusion appears to be supported by the following coagulation experiments with zirconium hydroxide sol :—

ZrO_2 = 10·34 g. per litre. Cl_2 = 0·7506 g. per litre.

Sol.	Amount taken (c.c.)	Total volume (c.c.)	Amount of KCl for coagulation.	Electrolyte for coagulation.	Ratio of KCl to chromate or dichromate.
$Zr(OH)_4$	1	5	1·3 c.c. *N*/5	1·4 c.c. *N*/125-K_2CrO_4	23·2
,,	1	5	1·3 c.c. *N*/5	2·2 c.c. *N*/125-$K_2Cr_2O_7$	14·8

Metalic Hydroxides.

From the electric conductivity, viscosity and cataphoretic measurements and other considerations it has been shown in these laboratories (*Faraday Soc. Discussion*, October, 1920 ; *J. Phys. Chem.*, 1923, **27**, 376 ; *Chem. News*, 1926, **133**, 177 ; *Z. anorg. Chem.*, 1926, **152**, 405 ; 1928, **174**, 1) that when hydroxides of chromium, zinc, aluminium, tin, lead, beryllium, etc., are dissolved in sodium or potassium hydroxide they exist mainly as negatively charged colloids. We have determined the coagulating power of potassium hydroxide alone and potassium hydroxide containing different amounts of hydroxides of zinc, tin, aluminium, chromium and lead.

Hydroxides of these metals were prepared in cold and washed very carefully to free them from any electrolyte, and dissolved in the solution of potassium hydroxide. Then its coagulating power with a ferric hydroxide sol was determined. Similarly the coagulating power of potassium hydroxide alone was found. The experimental results are recorded below :—

Sol.	Hydroxide.	Concentration of the metallic hydroxide (g. per litre).	Amount of KOH (c.c.)	Amount of hydroxide added (c.c.)	Electrolyte for coagulation.	Concentration required.	Ratio to KCl.
$Fe(OH)_3$ containing 11·45 gms. of Fe_2O_3 in a litre.					KCl	1·5 c.c. $N/5$	1
					KOH	0·5 c.c. $N/63·77$	38·26
,,	$Zn(OH)_2$	11·792 ZnO	10	10	Zincate (on the assumption that no KOH formed zincate).	0·8 c.c. $N/102·04$	38·26
,,	$Sn(OH)_4$	4·8 SnO_2	10	10	Stannate conc. on the above assumption.	0·8 c.c. ,,	38·26
	$Al(OH)_3$	2·84 Al_2O_3	10	10	Aluminate conc. on the above assumption.	0·8 c.c. ,,	38·26
,,	$Cr(OH)_3$	8·92 Cr_2O_3	10	10	Chromate conc. as above.	0·8 c.c. ,,	38·26
$Fe(OH)_3$ containing 4·28 gms. of Fe_2O_3 per litre.					KCl	0·6 c.c. $N/10$	1
					KOH	1·3 c.c. $N/127·5$	58·8
	$Pb(OH)_4$	22·3 PbO_2	10		Plumbate conc. as above.	6 c.c. $N/510·2$	51

The experimental results show that the coagulating power of KOH does not change appreciably on the addition of the hydroxides of zinc, tin, lead chromium and aluminium. Hence these hydroxides appear to exist in the colloidal state in KOH. If zincate, plumbite etc. were formed the coagulating power of the solutions containing hydroxides would have been different from that of caustic potash itself.

Summary.

(1) In the case of hypophosphorous acid, electric conductivity and coagulation experiments with sodium hypophosphite show that the acid is monobasic with slight tendency to be dibasic, while in case of phosphorous acid although the results support the view that the acid is mainly dibasic with a slight tendency to be tribasic, it contradicts the view of Italiener that it exists as $(H_3PO_3)_2$ and ionises as $H_6P_2O_6 \rightleftharpoons 2H^{\circ} + H_4P_2O_6''$.

(2) The view that the iodates exist partially in the polymerised state has been supported from conductivity measurements and coagulation experiments.

(3) Coagulation results with sodium or potassium salts of antimonic, titanic, boric, vanadic, tungstic, and molybdic acids show the bivalent nature of their negative ions.

(4) The coagulation experiments with chromates and dichromates are in favour of the view that chromic acid in solution exists mainly as H_2CrO_4 and potassium dichromate as $KHCrO_4$.

(5) The view that when the hydroxides of chromium, zinc, aluminium, tin, lead, beryllium etc., are dissolved in sodium or potassium hydroxide, they exist mainly as negatively charged colloids has been supported from the coagulation experiments with ferric hydroxide sol.

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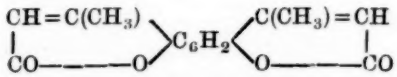
Coumaro-α-pyrones

By Rajendra Nath Sen and Duhkhaharan Chakravarti.

Hantzsch and Zürcher (*Ber.*, 1887, **20**, 1329) obtained in extremely poor yield dimethylcoumaro-α-pyrone (I), which they called dimethyldicoumarin, by condensing one molecule of resorcinol with two molecules of acetoacetic ester in one operation in the presence of concentrated sulphuric acid.

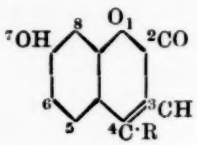


(I)

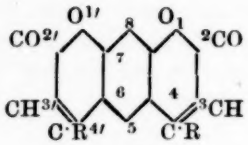
While engaged in a study of the reactivity of the substituted phenols in the formation of coumarins by Pechman's method, the present authors noticed that resorcinol and other polyhydroxy phenols do not condense satisfactorily with two molecules of acetoacetic ester or malic acid simultaneously ; but the pure hydroxycoumarins (from one molecule of each of the reactants) may be made to react under proper conditions with a second molecule of acetoacetic ester or malic acid producing coumaro-α-pyrones of Hantzsch and Zürcher type with much better yield. It has also been noticed incidentally that the hydroxycoumarins react more readily with malic acid than with acetoacetic ester (yield, 40-70%) even at the temperature of the water-bath, though the condensation of ordinary aromatic hydroxy compounds with malic acid generally requires a much higher temperature.

The monohydroxycoumarins, used for the synthesis of the coumaro-α-pyrones in this paper, have been obtained by the condensation of resorcinol and orcinol with (*i*) malic acid (Pechman, *Ber.*, 1884, **17**, 929 ; Pechman and Welsh, *Ber.*, 1894, **17**, 1646) and (*ii*) acetoacetic ester (Pechman and Duisberg, *Ber.*, 1883, **16**, 2119 ; Pechman and Cohen, *Ber.*, 18 '4, **17**, 2187). Umbelliferone (from resorcinol and malic acid) gives the coumaro-α-pyrone (III) or (IV) with malic acid ; while 4-methylumbelliferone

(from resorcinol and acetoacetic ester) produces (*i*) 4-methylcoumaro-α-pyrone with malic acid and (*ii*) 4:4′-dimethylcoumaro-α-pyrone with acetoacetic ester. Supposing the hydroxycoumarins derived from resorcinol to be 7-hydroxycoumarins (II) in accordance with Pechman's view (*Ber.*, 1884, **17**, 929), the corresponding coumaropyrones may have one of the two possible structures (III or IV).



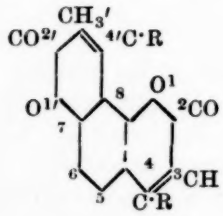
(II)



(III)

Coumaro-7:6-α-pyrone.

or



(IV)

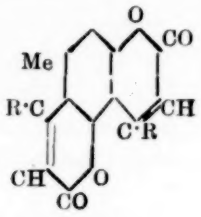
Coumaro-7:8-α-pyrone.

The first number following the word 'coumaro' refers to the carbon atom in the benzene nucleus to which the oxygen in the second pyrone ring is attached.

Attempt to settle between these two structures by the oxidation of the simple coumaropyrones with alkaline potassium permanganate proved unsuccessful.

Similarly two different structures are also possible for the coumaropyrones derived from orcinol, if the hydroxyl group in these hydroxycoumarins occupy the position 7; but assuming these hydroxycoumarins to be 5-hydroxycoumarins, as suggested by Dey (*J. Chem. Soc.*, 1915, **107**, 1614), the coumaropyrones (V) from orcinol will admit of only one structure. Thus homoumbelliferone (from orcinol and malic acid) gives 7-methylcoumaro-5:6-α-pyrone with malic acid; while 4-methylhomoumbelliferone (from orcinol and acetoacetic ester) produces (*i*) 4:7-di-

methylcoumaro-5:6-α-pyrone with malic acid and (*ii*) 4:4′:7-trimethylcoumaro-5:6-α-pyrone with acetoacetic ester.

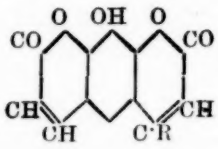


(V)

7-Methylcoumaro-5:6-α-pyrone.

The hydroxycoumarin, derived from hydroquinone (*Ber.*, 1884, **17**, 1649) could not be further condensed with acetoacetic ester or malic acid; while the attempt to prepare a hydroxycoumarin from catechol has not been successful.

The dihydroxycoumarins, derived from pyrogallol and phloroglucinol by their condensation with one molecule of acetoacetic ester or malic acid (Pechman, *loc. cit.*; Pechman and Cohen, *loc. cit.*; Pechman and Duisberg, *loc. cit.*) have also been made to react further with a second molecule of malic acid at the temperature of the water-bath, yielding monohydroxycoumaro-α-pyrones. Daphnetin (from pyrogallol and malic acid) and 4-methyldaphnetin (from pyrogallol and acetoacetic ester) condense with malic acid producing respectively 8-hydroxycoumaro-7:6-α-pyrone and 4-methyl-8-hydroxycoumaro-7:6-α-pyrone (VI).

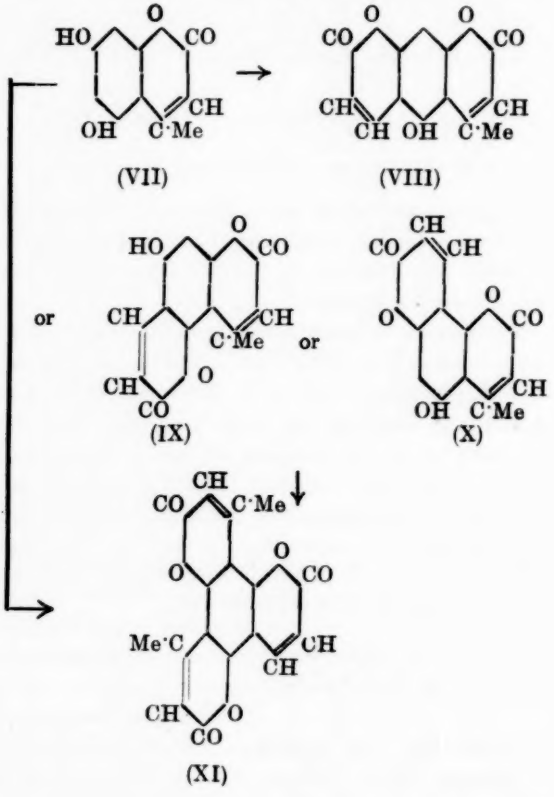


(VI)

It is remarkable that the dihydroxycoumarins, derived from pyrogallol, do not react further with acetoacetic ester, although they react readily with malic acid.

The condensation of phloroglucinol with acetoacetic ester gives a dihydroxycoumarin (VII), which with malic acid may lead to the formation of a coumaro-α-pyrone having any one of the following

possible structures (VIII, IX or X) ; but as Hantzsch and Zürcher (*loc. cit.*) have shewn that the hydroxycoumarin from phloroglucinol and acetoacetic ester by further reaction with acetoacetic ester forms a coumaro-dipyrone (XI) the formation of which follows best from structures (IX) or (X) for the coumaropyrone, the structure (VIII) is therefore excluded.



The coumaro-α-pyrones, the mono-, di-, and tri-methylcoumaro-α-pyrones, the hydroxy- and the hydroxy-methylcoumaro-α-pyrones, thus synthesised, are a series of a new type of interesting compounds. They are all difficultly soluble, fine, crystalline substances with high melting points. They all dissolve in hot caustic alkali solutions, the lactone rings being broken up ; and excepting those containing a free hydroxyl group, they are almost in-

soluble in ammonia, while they all remain practically unaffected by sodium carbonate and bicarbonate solutions in the cold; both the lactone rings being thus quite stable like that of coumarin itself. Excepting those coumaro-a-pyrones in which both 4 and 4′ positions are substituted by methyl groups, all these coumaro-a-pyrones dissolve in hot sodium bisulphite solutions (*cf.* Dey, *J. Chem. Soc.*, 1924, **125**, 554). The hydroxycoumaro-a-pyrones form mono-acetyl derivatives. Qualitative tests indicate the formation of nitration and sulphonation products of those compounds. Further study of the derivatives of these new coumaro-a-pyrones is in progress.

The condensations of the hydroxycoumarins with acetone dicarboxylic acid have also led to the formation of coumaro-a-pyrone-acetic acids, which will be the subject of a future communication.

Experimental.

Coumaro-7:6 (*or* 7:8-)-a-*pyrone*.—An intimate mixture of umbelliferone (4 g.) (*Ber.*, 1884, **17**, 929), malic acid (4 g.) and sulphuric acid (*d* 1·84, 12 c. c.) is heated on the water-bath. Effervescence soon begins and the solution assumes a deep-red colour. The solution is heated until the effervescence ceases (3-4 hours) and is then poured into powdered ice, when a red coloured precipitate is obtained. The precipitate is then filtered off, digested with ammonia to remove any unchanged umbelliferone and is crystallised from glacial acetic acid (yield, 60%). It forms reddish-yellow leaflets, m. p. 245-250°, almost insoluble in ether and chloroform, sparingly soluble in alcohol and acetone and moderately soluble in hot glacial acetic acid. It is almost insoluble in ammonia and sodium carbonate solution, but soluble in hot caustic alkalis (reddish solution) without any fluorescence. (Found: C, 66·9, 67·1 ; H, 3·2, 3·1. $C_{12}H_6O_4$ requires C, 67·29; H, 2·8 per cent.).

7-*Methylcoumaro*-5:6-a-*pyrone*.—A solution of homoumbelliferone (3·5 g.) (*Ber.*, 1884, **17**, 1646) and malic acid (3·5 g.) in concentrated sulphuric acid (10 c. c.) is heated for about two hours on the water-bath until effervescence ceases. The method of purification of the compound is the same as in the previous case (yield, 50%). It forms greyish silky needles from glacial acetic acid, m. p. 318-320° with slight decomposition; sparingly soluble in ether, hot chloroform, benzene ; moderately soluble in boiling alcohol and acetone and

almost insoluble in ammonia and sodium carbonate solution, but dissolves in hot caustic alkalis without fluorescence. (Found: C, 68·4 ; H, 3·7. $C_{13}H_8O_4$ requires C, 68·42 ; H, 3·5 per cent.)

4-Methylcoumaro-7:6 (or 7:8)-α-pyrone.—A solution of 4-methylumbelliferone (10 g.) (*Ber.*, 1883, **16**, 2119) and malic acid (10 g.) in concentrated sulphuric acid (30 c. c.) is heated on the water-bath for 2—3 hours until the effervescence ceases. The method of purification of the compound is the same as in the previous cases (yield, 70%). It forms thin silky needles from a mixture of acetone and chloroform (1:3) and micro-crystalline from hot glacial acetic acid; m. p. 304-5°. It is almost insoluble in ether or benzene, sparingly soluble in alcohol and acetone ; moderately soluble in chloroform and very slightly soluble in hot ammonia with a yellow colouration. No fluorescence in alkaline solution. (Found: C, 68·0 68·2 ; H, 3·8, 3·9. $C_{13}H_8O_4$ requires C, 68·42; H, 3·5 per cent.).

4:7-Dimethyl-coumaro-5:6-α-pyrone.—A mixture of 4-methylhomoumbelliferone (5 g.) (*Ber.*, 1884, **17**, 2187), malic acid (5 g.) and concentrated sulphuric acid (15 c. c.) is heated on the water-bath for about three hours until the effervescence ceases. The solution is then poured into water, the precipitate is filtered, dried, and digested with boiling absolute alcohol. The residue is finally crystallised from a mixture of acetic acid and acetic anhydride (3:1) (yield, 65%). It forms beautiful, colourless, thin, silky needles, m. p. 310-313°, difficultly soluble in the organic solvents, insoluble in ammonia, soluble in hot caustic alkalis without any fluorescence. (Found: C, 69·1; H, 4·2. $C_{14}H_{10}O_4$ requires C, 69·42; H, 4·1 per cent.).

4:4'-Dimethylcoumaro-7:6 (or 7:8-)-α-pyrone.—A mixture of 4-methylumbelliferone (10 g.), acetoacetic ester (10 c. c.) and concentrated sulphuric acid (30 c. c.) is kept for about a week. The solution is then poured into water, the precipitate is filtered off, digested with hot ammonia to remove the unchanged 4-methylumbelliferone and is finally crystallised from a large quantity of boiling alcohol. Yield about 30%. It forms snow-white micro-crystalline unmeltable solid, almost insoluble in the ordinary organic solvents, slightly soluble in ammonia with a yellow colour, soluble in hot caustic alkalis without any fluorescence. (Found: C, 69·31 ; H, 4·4. $C_{14}H_{10}O_4$ requires C, 69·42; H, 4·1 per cent.).

This compound is identical in properties with the dimethyldicoumarin of Hantzsch and Zürcher (*loc. cit.*).

4:4′: 7-*Trimethylcoumaro*-5: 6-α-*pyrone*.—4-Methylhomoumbelliferone (15 g.), acetoacetic ester (18 c. c.) and concentrated sulphuric acid (40 c. c.) are mixed together in the cold and the solution kept for several days. The solution is then poured into powdered ice, the precipitate filtered off and digested with boiling rectified spirit. The residue is finally crystallised from a large quantity of boiling alcohol. Yield not more than 15%; colourless micro-crystalline unmeltable powder, soluble with difficulty in boiling alcohol and acetone and almost insoluble in many organic solvents. (Found: C, 70·18; H, 4·9. $C_{15}H_{12}O_4$ requires C, 70·31; H, 4·7 per cent.).

8-*Hydroxycoumaro*-7:6-α-*pyrone*.—A mixture of daphnetin (4 g.) (*Ber.*, 1884, **17**, 929), malic acid (4 g.) and concentrated sulphuric acid (9 c. c.) is heated on the water bath for 3-4 hours till the effervescence ceases. The solution is then poured into water, the precipitate filtered, dried and digested with hot absolute alcohol. The residue is then finally crystallised from pyridine, containing a few drops of water (yield, 40%). It is a greyish microcrystalline substance, very difficutly soluble in boiling alcohol, acetone and pyridine; almost insoluble in ether, benzene, and chloroform and sodium carbonate solution, soluble in ammonia and hot caustic alkalis. (Found: C, 62·35; H, 2·8. $C_{12}H_6O_5$ requires C, 62·6; H, 2·6 per cent.).

4-*Methyl*-8-*hydroxycoumaro*-7:6-α-*pyrone*.—A solution of 4-methyldaphnetin (9·5 g.) (*Ber.*, 1884, **17**, 2187) and malic acid (7 g.) in sulphuric acid (20 c. c.) is heated on the water-bath till the effervescence ceases. The method of purification of the compound is the same as in the previous case. It is finally crystallised from pyridine. Yield 55%. It forms almost colourless rectangular plates, very sparingly soluble in alcohol, acetone, ether, benzene and chloroform; readily soluble in pyridine, soluble in ammonia and caustic alkalis. (Found: C, 63·7; H, 3·4. $C_{13}H_8O_5$ requires C, 63·93; H, 3·28 per cent.).

The *mono-acetyl* derivative, prepared in the usual manner and cryrtallised from a large quantity of boiling alcohol, is a greyish powder without any melting point. (Found: C, 62·7; H, 3·7. $C_{15}H_{10}O_6$ requires C, 62·93; H, 3·5 per cent.).

5-*Hydroxycoumaro*-7:8-α-*pyrone* or 7-*Hydroxycoumaro*-5:6-α-*pyrone*.—A mixture of 4-methyl-5:7-dihydroxycoumarin (9·5 g.) (*Ber.*, 1884, **17**, 2187) and malic acid (6 g.) and sulphuric acid

(20 c. c.) is heated on the water-bath for 3-4 hours till the effervescence ceases. The solution is then poured in ice, the precipitate filtered and dissolved in ammonia. The ammoniacal solution is acidified with hydrochloric acid and the precipitate thus obtained is crystallised from pyridine. Yield, 60% ; colourless thin silky needles, decomposing at 320° ; it is sparingly soluble in boiling alcohol, moderately soluble in pyridine, soluble in ammonia with a yellow colour. (Found: C, 64·15; H, 3·4. $C_{13}H_8O_5$ requires C, 63·93; H, 3·28 per cent.).

The *mono-acetyl* derivative, crystallised from pyridine, is a colourless micro-crystalline powder. (Found: C, 62·7; H, 3·8. $C_{15}H_{10}O_6$ requires C, 62·93; H, 3·5 per cent.).

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Phosphorus Oxychloride as a Condensing Agent in the Synthesis of Coumarin Derivatives.

By K. G. Naik, R. D. Desai and R. K. Trivedi.

The subject of the present communication arose from an attempt to condense benzylacetoacetic ester with β-naphthol in presence of concentrated sulphuric acid as the condensing agent. The expected coumarin 3-benzyl-4-methyl-1:2-β-naphthopyrone was not obtained, but methylindene-carboxylic acid was produced by the internal condensation of the ester. α-Naphthol was however, condensed under identical conditions by Ghosh and Jacobson to give the corresponding pyrone derivative (*J. Chem. Soc.*, 1915, **107**, 424). But on repeating the condensation under the conditions outlined therein, we failed to get the product obtained by them. When concentrated sulphuric acid was replaced by phosphorus oxychloride as the condensing agent, α-naphthol condensed very readily with benzylacetoacetic ester giving the coumarin derivative.

Equimolecular quantities of the phenol and benzylacetoacetic ester were mixed with phosphorus oxychloride (about 0·5 gm. for 2 gms. of the mixture) and the whole heated on the water-bath for about an hour. The mixture was then poured into water, when a solid product separated which was subsequently purified from alcohol.

In each case, excellent yields of crystalline products were obtained. From the physical properties and the melting points of their derivatives, as shown in the adjoining table, the products appeared to be identical with those of Ghosh and Jacobson.

Products obtained from various phenols and benzyl-acetoacetic ester.

	Phenols.	Resorcinol.	α-Naphthol.	Pyrogallol.	Phloroglucinol.
Observations by Ghosh & Jacobson.	Crystalline form	Short, yellow glistening prisms.	Yellow needles	—	Hard, short needles.
	M.p. ...	224°	187°	185°	218°
	M.p. of acetyl derivative ...	168°	—	172°	154°
	M.p. of benzoyl derivative ...	150°	—	184°	—

Observations by the authors.

Phenols.	Resorcinol.	α-Naphthol.	Pyrogallol.	Phloroglucinol.
Crystalline form	Colourless, glistening prisms.	Pale yellow, slender needles.	Colourless, glistening plates.	Short needles.
M.p. ...	225°	189°-90°	193°	227°
M.p. of acetyl derivative ...	171°	—	172°	158°-59°
M.p. of benzoyl derivative ...	160°	—	181°	124°-25°

THE COLLEGE,
BARODA.

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Dissociation Constants of some Inorganic Acids from Solubility Measurements.

By W. V. Bhagwat and N. R. Dhar.

In previous papers (*Z. Elektrochem.*, 1913, **19**, 407 ; *J. Amer. Chem. Soc.*, 1913, **35**, 800 ; *J. Chem. Soc.*, 1915, **107**, 824 ; *Z. anorg. Chem.*, 1926, **153**, 323 ; *J. Indian Chem. Soc.*, 1928, **5**, 585), we have shown that the dissociation constants of weak acids can be calculated from the measurements of the solubility of sparingly soluble weak acids (*e.g.*, benzoic, cinnamic, boric, arsenious, carbonic, etc.) in sodium or potassium salts of the acids of which we want to determine the dissociation constants.

In this communication we are recording the results of solubility measurements with benzoic, carbonic, arsenious and boric acids in sodium or potassium salts of hypophosphorous, phosphorous, chromic, hydrofluoric, iodic, titanic, antimonic, boric, vanadic, tungstic and molybdic acids.

From these solubility measurements we can get an idea about the dissociation constants of these acids. Moreover, we have critically discussed the principle of this method of determining the dissociation constants of acids and deduced a general formula.

The experimental results are recorded in the following tables, where a = solubility of the sparingly soluble acid in water, b = the solubility of the same acid in sodium or potassium salt of the acid of which the dissociation constant has to be determined, c = original concentration of the salt solution, K = dissociation constant of the unknown acid, and K_1 = dissociation constant of the known acid. In the case of the dibasic acids, only the second dissociation constants are obtained by this method (*cf.* Datta and Dhar, *J. Chem. Soc.*, 1915, **107**, 824).

Table I.

Hypophosphorous Acid (*Sodium Hypophosphite Solution used*).

(i) *Dissociation constant with benzoic acid* ($K_1 = 6 \times 10^{-5}$) *at* 17°.

a	b	c	$b-a$	$c-b+a$	K
0·0220	0·0350	0·8454	0·0130	0·8323	$6·5 \times 10^{-3}$
,,	0·0320	0·5918	0·0100	0·5818	$7·6 \times 10^{-3}$
,,	0·0300	0·4227	0·008	0·4147	$8·5 \times 10^{-3}$
,,	0·0270	0·2536	0·005	0·2486	$1·3 \times 10^{-2}$

(ii) *With carbonic acid gas* ($K_1 = 3 \times 10^{-7}$).

Temp.	*a*	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
27°	0·06204	0·0703	0·1467	0·00826	0·1384	$3·7 \times 10^{-5}$
25°	0·06582	0·08554	0·9698	0·01972	0·95008	$4·2 \times 10^{-5}$
,,	,,	0·0786	0·4849	0·01278	0·4721	$5·7 \times 10^{-5}$
,,	,,	0·0745	0·2424	0·00868	0·2337	6×10^{-5}

The above results are sufficient to indicate that the dissociation constant increases with the fall of concentration of salt solutions. The dissociation constant with carbon dioxide has a much smaller value than with benzoic acid. Hence the dissociation constant appears to be lowered as a weaker acid is used for determining the dissociation constant.

These results show that hypophosphorous acid is stronger than phosphorous acid. This relation is also observable from the following electric conductivity measurements:—

TABLE II.

Dilution	16	32	64	128	256	512	1024
Molecular conductivity (H_3PO_2)	245	281	312	335	352	361	367
Molecular conductivity (H_3PO_3)	222	257	292	318	337	351	358

(Mellor—'Inorganic & Theoretical Chemistry," 1928, Vol. VIII, p. 902).

TABLE III.

Phosphorous Acid (Sodium Phosphite Solution used.)

(i) *Dissociation constant with benzoic acid at* 17°.

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
0·0220	0·4860	1·8060	0·4640	1·3420	$8·25 \times 10^{-6}$
,,	0·2930	0·9030	0·2710	0·6320	$1·13 \times 10^{-5}$
,,	0·2490	0·7224	0·2270	0·4954	$1·27 \times 10^{-5}$
,,	0·1710	0·4515	0·1490	0·3025	$1·79 \times 18^{-5}$

(ii) *Dissociation constant with carbonic acid.*

Temp.	*a*	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
24°	0·0679	0·2337	0·7692	1·1658	0·60	$4\cdot4\times10^{-7}$
,,	,,	0·2055	0·3846	0·1376	0·2469	$2\cdot8\times10^{-7}$
21°	0·07454	0·2295	0·6153	0·1549	0·4604	$4\cdot2\times10$
,,	,,	0·1945	0·4615	0·1199	0·3415	$5\cdot1\times10^{-7}$
25·5°	0·0630	0·2322	2·2015	0·1692	2·0323	$1\cdot3\times10^{-7}$

TABLE IV.

Chromic Acid.

(i) *Dissociation constant with carbonic acid at* 30° *(assuming complete ionisation of potassium dichromate).*

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
0·05714	0·3684	1·000	0·3112	0·6880	$1\cdot9\times10^{-7}$
,,	0·2601	0·500	0·2029	0·2971	$1\cdot28\times10^{-7}$
,,	0·1973	0·250	0·1402	0·1098	$9\cdot5\times10^{-8}$
,,	0·1500	0·1250	0·0928	0·0322	$6\cdot4\times10^{-8}$
,,	0·2541	0·3962	0·1970	0·1992	$8\cdot6\times10^{-8}$
,,	0·2460	0·3482	0·1880	0·1594	$7\cdot6\times10^{-8}$
,,	0·2637	0·4309	0·2066	0·2243	$9\cdot0\times10^{-8}$
,,	0·1760	0·2154	0·1188	0·0966	$1\cdot1\times10^{-7}$
,,	0·2143	0·2396	0·1572	0·0824	$5\cdot7\times10^{-8}$

We have also worked with benzoic and boric acids. In the case of arsenious acid, the solution becomes green due to the reduction of the chromate. With benzoic, the chromate was converted into dichromate.

(ii) *Dissociation constant with boric acid at* 30° (K_1 *for boric acid* $=6\cdot4\times10^{-10}$, Lunden, *J. Chim. phys.*, 1907, **5**, 10 ; ($K_1=5\cdot7\times10^{-10}$, Menzel, *Z. physikal. Chem.*, 1922, **100**, 295.)

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
1·029	1·238	0·1017	0·209	Nagative	...
,,	1·213	0·09457	0·184	Negative	...
,,	1·133	0·04728	0·084	Negative	...
,,	1·035	0·01017	0·006	·00147	$7\cdot6\times10^{-8}$
	1·035	0·009457	0·006	·0003457	$6\cdot3\times10^{-8}$

The above and other negative results will be discussed later on. Hence the second dissociation constant of chromic acid is very small.

(iii) *Dissociation constant with benzoic acid at* 30°.

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
0·03147	0·1145	0·1704	0·08303	0·08737	$3·1 \times 10^{-5}$
,,	0·08514	0·1155	0·05367	0·06183	4×10^{-5}
,,	0·0841	0·1076	0·05263	0·05497	$3·7 \times 10^{-5}$
,,	0·06152	0·1017	0·05005	0·05165	$3·8 \times 10^{-5}$
,,	0·0774	0·09457	0·04593	0·04864	$4·3 \times 10^{-5}$
,,	0·06812	0·0742	0·03665	0·03755	$5·2 \times 10^{-5}$
,,	0·06295	0·06531	0·03148	0·03383	6×10^{-5}

It is to be observed that *K* by this method has much larger value than that obtained with carbon dioxide. Also the dissociation constant increases with the dilution.

TABLE V.

Hydrofluoric Acid (Potassium Fluoride Solution used).

(i) *Dissociation constant with benzoic acid at* 30°.

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
0·03204	0·1361	1·191	0·1040	1·0870	$1·88 \times 10^{-4}$
,,	0·1168	0·9528	0·08476	0·8680	$2·9 \times 10^{-4}$
,,	0·09689	0·7146	0·06485	0·6498	$2·9 \times 10^{-4}$
,,	0·07442	0·4764	0·04238	0·4337	$3·2 \times 10^{-4}$
0·03147	0·04231	0·04017	0·01084	0·02933	$4·7 \times 10^{-4}$
,,	0·04076	0·02678	0·00929	0·01749	$3·6 \times 10^{-4}$

(ii) *Dissociation constant with boric acid at* 30°.

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
1·029	1·566	0·3287	0·537	Negative	*x*
,,	1·330	0·1643	0·301	,,	*x*
,,	1·205	0·08217	0·176	,,	*x*

(iii) *Dissociation constant with arsenious acid at* 30°.

(Compare von Zawidzki, *Ber.*, 1903, **36**, 1427 ; $K_1 = 2 \times 10^{-10}$).

a	b	c	$b-a$	$c-b+a$	K
0·0284	0·2936	0·08215	0·0096	0·07257	$2·2 \times 10^{-5}$
,,	0·3026	0·1643	0·0186	0·1557	$1·27 \times 10^{-5}$
,,	0·3096	0·3287	0·0256	0·3031	$1·28 \times 10^{-5}$

(iv) *Dissociation constant with carbonic acid gas.*

Temp.	a	b	c	$b-a$	$c-b+a$	K
28°	0·06127	0·1504	1·238	0·08913	1·1488	$2·6 \times 10^{-5}$
,,	,,	0·1295	0·619	0·06823	0·5508	$2·2 \times 10^{-5}$
30°	0·05714	0·1320	0·9904	0·07486	0·9155	$3·0 \times 10^{-5}$
,,	,,	0·1156	0·7428	0·05846	0·6843	$3·7 \times 10^{-5}$

It will be seen that in all these cases dissociation constant increases with dilution and weaker the acid used, the smaller is the dissociation constant obtained with it. Hence hydrofluoric acid is much weaker than the other halogen acids.

TABLE VI.

Iodic Acid (*Potassium Iodate Solution was used*).

(i) *Dissociation constant with carbonic acid at* 19°.

a	b	c	$b-a$	$c-b+a$	K
0·07886	0·08373	0·3437	0·00487	0·3388	$3·88 \times 10^{-4}$
,,	0·08164	0·13748	0·00278	0·1347	$4·1 \times 10^{-4}$
0·08641 (18°)	0·09505	0·6874	0·00864	0·67876	$2·1 \times 10^{-4}$

Hence iodic acid appears to be weaker than chloric acid, because the solubility of carbon dioxide in a solution of potassium chlorate is the same as in water. There was no increase in the solubility of benzoic acid in solutions of potassium iodate.

TABLE VII.

Titanic Acid (*Potassium Titanate Solution used*).

Kahlbaum's potassium titanate was washed with alcohol to remove any free alkali. The salt is only sparingly soluble in water and the solution is alkaline indicating that it is appreciably hydrolysed.

(i) *Dissociation constant with benzoic acid at* 18°.

a	b	c	$b-a$	$c-b+a$	K
0·0226	0·0240	0·00550	0·0014	0·00410	$2·8\times10^{-3}$
,,	0·0234	0·004125	0·0008	0·003325	$7·0\times10^{-3}$
,,	0·0232	0·00275	0·0006	0·002150	$8·1\times10^{-3}$
,,	0·0230	0·001375	0·0004	0·000975	$8·2\times10^{-3}$

The dissociation constant increases with dilution. It is to be observed that the saturated solution of potassium titanate has the strength about $N/200$.

(ii) *Dissociation constant with carbonic acid.*

a	b	c	$b-a$	$c-b+a$	K
0·07886 (19°)	0·1149	0·0050	0·0361	Negative	x
0·08377(17°)	0·09585	0·0035	0·01208	,,	x
,,	0·08854	0·0015	0·00477	,,	x

Due to the alkaline nature of the solution of potassium titanate the solubility of carbonic acid gas is tremendously increased giving rise to negative results. Hence titanic acid appears to be a comparitively weak acid. No electric conductivity measurement is, however, available for this acid.

TABLE VIII.

Antimonic Acid (Solution of $K_2H_2Sb_2O_7$ *was used).*

(i) *Dissociation constant with benzoic acid at* 18°.

a	b	c	$b-a$	$c-b+a$	K
0·0226	0·0240	0·010	0·0014	0·0086	$5·9\times10^{-3}$
,,	0·0237	0·0075	0·0011	0·0064	$7·1\times10^{-3}$
,,	0·0234	0·0050	0·0008	0·0042	$8·9\times10^{-3}$
,,	0·0230	0·0025	0·0004	0·0021	$1·78\times10^{-2}$

This salt is sparingly soluble and the saturated solution at 18° has the strength about $N/50$. From the dissociation constant it is clear that it increases as in previous cases with dilution.

(ii) *Dissociation constant with carbonic acid gas.*

Temp.	a	b	c	$b-a$	$c-b+a$	K
20°	0·07654	0·09173	0·020	0·01519	0·00481	$4·79\times10^{-7}$
21°	0·07432	0·08191	0·010	0·00759	0·00241	$9·3\times10^{-7}$
22°	0·07213	0·07682	0·005	0·00469	0·00031	$2·9\times10^{-7}$

Antimonic acid also appears to be a weak acid.

TABLE IX.

Boric Acid (Borax was used).

(i) *Dissociation constant with benzoic acid at* 18°.

a	b	c	$b-a$	$c-b+a$	K
0·0226	0·710	0·4	0·6874	Negative	x
,,	0·540	0·3	0·5174	,,	x
,,	0·380	0·2	0·3574	,,	x
,,	0·180	0·1	0·1574	,,	x

(ii) *Dissociation constant with carbonic acid gas.*

Temp.	a	b	c	$b-a$	$c-b+a$	K
16°	0·08641	0·4213	0·2156	0·3349	,,	x
16°	0·08641	0·2664	0·0924	0·1800	,,	x
17°	0·08377	0·3470	0·1540	0·2633	Negative	x
18°	0·08123	0·5288	0·3080	0·4457	,,	x

These negative results with boric acid show that it is a very weak acid, and these solubility measurements support the conclusion from electric conductivity determination.

TABLE IX.

Vanadic Acid (Sodium Vanadate Solution used).

In case of carbonic acid gas we get negative results and the solution of vanadate which was originally colourless becomes yellow due to the liberation of vanadic acid.

(i) *Dissociation constant with benzoic acid at 17°.*

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
0·0220	0·02825	0·1247	0·00625	0·11845	4×10^{-3}
,,	0·02600	0·09345	0·0040	0·08945	$7·4 \times 10^{-3}$
,,	0·02450	0·06235	0·0025	0·05985	$1·26 \times 10^{-3}$
,,	0·02350	0·03117	0·0015	0·02967	$1·74 \times 10^{-3}$

The dissociation constant goes on increasing with dilution.

(ii) *Dissociation constant with carbonic acid gas at 21°.*

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
0·07427	0·7177	0·4646	0·6434	Negative	*x*
,,	0·5944	0·3117	0·5201	,,	*x*

Table X.

Tungstic Acid (Sodium Tungstate Solution used).

(i) *Dissociation constant with benzoic acid at 30°.*

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
0·03204	0·07207	0·09980	0·04003	0·05977	$7·1 \times 10^{-5}$
,,	0·06935	0·09050	0·03731	0·05319	$7·3 \times 10^{-5}$
,,	0·06646	0·08014	0·03442	0·04572	$7·4 \times 10^{-5}$
,,	0·07287	0·1012	0·04083	0·06086	$6·96 \times 10^{-5}$
,,	0·06046	0·06072	0·02842	0·03232	$7·6 \times 10^{-5}$
,,	0·04738	0·0253	0·01520	0·01010	$7·4 \times 10^{-5}$

(ii) *Dissociation constant with arsenious acid at 30°.*

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
0·284	0·[illegible]481	0·08014	0·2641	Negative	*x*
,,	0·4331	0·04043	0·1491	Negative	*x*

Table XII.

Molybdic Acid.

(i) *Dissociation constant with carbonic acid in ammonium molybdate.*

Temp.	*a*	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
23°	0·0700	0·0841	0·500	0·01410	0·4857	$5·1 \times 10^{-5}$
22°	0·07213	0·0893	0·250	0·01717	0·2428	$1·2 \times 10^{-5}$
20·5°	0·07581	0·08654	0·125	0·01073	0·1142	$2·2 \times 10^{-5}$

(ii) *Dissociation constant with carbonic acid in potassium molybdate at 25°.*

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
0·06582	0·1686	0·4096	0·1027	0·3068	$5·7 \times 10^{-7}$
,,	0·1200	0·2048	0·05418	0·1506	1×10^{-6}
,,	0·0951	0·1024	0·02928	0·0781	$4·8 \times 10^{-6}$
,,	0·0802	0·04096	0·01438	0·0265	$3·6 \times 10^{-5}$

(ii) *Dissociation constant with benzoic acid in postassium molybdate solution at 30°.*

a	*b*	*c*	*b*−*a*	*c*−*b*+*a*	*K*
0·03204	0·06967	0·06568	0·03763	0·02805	$3·8 \times 10^{-5}$
,,	0·05766	0·03978	0 02562	0·01414	$4·1 \times 10^{-5}$
,,	0·04805	0·02386	0·01601	0·00785	$5·89 \times 10^{-5}$
,,	0·05365	0·03284	0·02161	0·01123	$4·62 \times 10^{-5}$
,,	0·08038	0·07729	0·04884	0·02848	$2·3 \times 10^{-5}$

It will be observed that as dilution increases, the dissociation constant also increases.

The foregoing experimental results obtained with vanadic, tungstic and molybdic acids show that they are weak acids. With molybdic acid Grossmann and Kramer (*Ber.*, 1903, **36**, 1606) obtained the following results:—

Dilution ...	16	32	64	128	256	512	1024
Molecular conductivity(25°)	95·8	129·5	147·5	155·6	160·6	163·6	169

Walden ("Das Leitvermögen der Elektrolyte," 1924, II, p. 117) has recorded the following results with tungstic acid at 25°:—

Dilution ...	32	64	128	256	512	1024
Molecular conductivity ...	176·4	233·5	279·1	325·2	371·6	416·7

It should be emphasised that all these acids in aqueous solutions exist partly in the colloidal state.

Discussion.

From the foregoing results it will be observed that—

(1) The formula $K=\frac{K_1 \times a\,(c-b+a)}{(b-a)^2}$ breaks down in some cases specially when the acid used for determining the dissociation constant is polybasic and that we get negative results.

(2) The dissociation constant goes on increasing with the dilution of the salt solution. In other words, the solubility of the acid falls off more rapidly than the concentration of the salt solution.

(3) The weaker the acid used, the lower is the value of the dissociation constant of the unknown acid.

In deducing the dissociation constants we have applied the formula

$$K = \frac{K_1 \times a\,(c-b+a)}{(b-a)^2}$$

The assumptions in this formula are:—

(*a*) The sodium or potassium salt is completely ionised.

(*b*) The acids of which the dissociation constants are K and K_1 are so weak that their ionisation is negligible.

Although the second assumption is generally true, the first is not exact and corrections are necessary.

The above formula has been deduced irrespective of the basicity of the acid of which K_1 we assume. From the viewpoint of the basicity of the acid the applicability of the formula is open to question and corrections are necessary. In deducing this formula we have considered the following equation:—

$$C_6H_5{\cdot}CO_2H + CH_3{\cdot}CO_2Na \rightleftarrows CH_3{\cdot}CO_2H + C_6H_5{\cdot}CO_2Na.$$

In the above relation the acids concerned are fortunately monobasic and we shall try to prove that the formula is specific for monobasic acids of which K_1 we assume, and it can be deduced from the general formula which will be considered now. The basicity of the acid of which dissociation constant is required has very little to do in changing the relation, provided it is assumed that the salt of this acid ionises completely and that the acids do not ionise, which is only partially true. We shall now proceed to derive a general formula.

Let the acid of which K_1 we assume be H_nB, where n is the basicity of the acid. Let H_mA be the acid whose dissociation constant is required, where m is its basicity.

Then the sodium salt of the acid H_nB will be Na_nB and of H_mA will be Na_mA, then

$$Na_mA + H_nB \rightleftarrows Na_{m-1}HA + H_{n-1}NaB$$

Let the solubility of H_nB in water $=a$ and in Na_mA solution of concentration $c=b$.

Let k_1, k_2, k_3 and k_4 be the degrees of ionisation of Na_mA, H_nB, $Na_{m-1}HA$ and $H_{n-1}NaB$ respectively.

Now the excess $=b-a$ of the acid H_nB dissolving in the solution of Na_mA of concentration c will ionise as

$$H_nB \rightleftarrows H_n + B^{1\cdots n}$$

or
$$\underset{(b-a)}{H_nB} \rightleftarrows \underset{(b-a)}{nH^\circ} + \underset{(b-a)}{B^{1\cdots n}}$$

Hence the concentration of H ions that go to form $H_{n-1}NaB$ will be $(b-a)/n$. Hence the concentration of $Na_{m-1}HA$ formed $=(b-a)/n$.

Now the dissociation constant of the acid H_nB is given by

$$K=\frac{H \times H_{n-1}B}{H_nB}$$

but as the solution is always saturated with H_nB, the concentration of $H_nB=a$. But a part of it also ionises and hence the concentration of H_nB undissociated

$$=H_nB-k_2H_nB=(1-k_2)H_nB=(1-k_2)a$$

Also the concentration of $H_{n-1}B$ will be given by $H_{n-1}NaB$, which will ionise as

$$H_{n-1}NaB \rightleftharpoons H_{n-1}B' + Na^\circ$$

Hence the concentration of $H_{n-1}B' = k_4(b-a)/n$.

$$K=\frac{H^\circ \times k_4(b-a)/n}{(1-k_2)a}$$

Hence
$$H^\circ=\frac{K \times (1-k_2)a}{\frac{k_4(b-a)}{n}}$$

The dissociation constant of the acid H_mA will be given by

$$K'=\frac{H^\circ \times H_{m-1}A'}{H_mA}$$

and hence
$$K'_n=\frac{H^\circ \times A'}{HA''}.$$

But the concentration of HA from $Na_{m-1}HA = k_3(b-a)/n$

because it ionises as $Na_{m-1}HA \rightleftharpoons Na^{\circ}_{m-1} + HA'$

Also the concentration of $A' = k_1c - k_3(b-a)/n$

because Na_mA ionises as $Na_mA \rightleftharpoons Na_m + A'$ and part of this forms $Na_{m-1}HA$, which $= k_3(b-a)/n$.

Hence substituting these values of H°, A' and HA we get the nth dissociation constant of the acid as

$$K'_n = \frac{K(1-k_2)a}{\frac{k_4(b-a)}{n}} \times \frac{k_1c - k_3\frac{(b-a)}{n}}{k_3\frac{(b-a)}{n}}$$

$$= \frac{nK(1-k_2)a[nk_1c - k_3(b-a)]}{k_4k_3(b-a)^2} \quad \ldots \quad (A)$$

If we introduce the conception that the salts are completely ionised and acids do not ionise at all, then

$$k_1 = k_3 = k_4 = 1, \text{ and } k_2 = 0.$$

Hence $$K_n' = \frac{n \times K \times a \times [nc - (b-a)]}{(b-a)^2} \quad \ldots \quad (B)$$

and if acids are monobasic as considered by Dhar and Philip we can put $n=1$, and get

$$K_n' = \frac{K \times a(c-b+a)}{(b-a)^2} \quad \ldots \quad (ii)$$

the same formula as has been used in the calculation of the experimental results.

Thus we have succeeded in deriving a general formula and proving that Dhar (*J. Amer. Chem. Soc.*, 1913, **35**, 800) and Philip's (*J. Chem. Soc.* 1905, **87**, 987; 1909, **95**, 1466) formulae can be derived from it as special cases.

It is quite clear that this method of finding dissociation constant is only approximate at least for the acids whose basicity is greater than one and whose dissociation constant we assume, and higher the basicity, the less accurate are the results. Because in deriving this

formula we assume $H_nB = nH^\circ + B'$ which is never realised ; but there are various probabilities of ionisation

$$H_nB \rightleftarrows H^\circ + [H_{n-1}B]'$$

$$H_nB \rightleftarrows 2H^\circ + [H_{n-1}B]''$$

$$H_nB \rightleftarrows nH^\circ + B'''^{\cdots n}$$

When $n=1$, the probability is only one and hence the calculated results are satisfactory.

In deriving the above general formula we have introduced the simplest conception. If we try to allow for all these probabilities the problem becomes very complex.

It is quite clear from the above formula why the formula

$$K' = \frac{K \times a(c-b+a)}{(b-a)^2}$$

breaks down when using carbonic acid gas, boric acid, arsenious acid etc., which are polybasic. If we employ the general formula in no case we get negative results. The correctness of the general formula is borne out by following results ... potassium fluoride and boric acid, potassium chromate and boric acid, potassium fluoride and arsenious acid, etc. In all these case, we have already shown that we get negative results by the simple formula of Dhar and Philip.* But our general formula gives positive and consistent results.

(i) *Dissociation constant of hydrofluoric acid with boric acid at* 30°.

$$K_1 = \frac{nK \times a(c-b+a)}{(b-a)^2}$$

But $n=3$ and $K=6{\cdot}4\times10^{-10}$.

Hence $K_1 = 3\times6{\cdot}4\times10^{-10}\times a\frac{(3c-b+a)}{(b-a)^2}$.

a	b	$3c$	$b-a$	$3c-b\times a$	$K\times10^{-9}$
1·029	1·566	0·9861	0·537	0·4491	1·05
,,	1·330	0·4930	0·301	0·1920	1·39
,,	1·205	0·2465	0·176	0·070	1·48

The dissociation constant increases with dilution.

(ii) *Dissociation constant of chromic acid with boric acid at* 30°.

$$K = \frac{3K' \times a \times (3c - b + a)}{(b - a)^2} \text{ for } n = 3.$$

a	b	$3c$	$b-a$	$3c-b+a$	$K \times 10^{-9}$
1·029	1·238	0·3051	0·209	0·0961	1·45
,,	1·213	0·2837	0·184	0·0997	1·94
,,	1·133	0·1418	0·084	0·0578	5·39

(iii) *Dissociation constant of hydrofluoric acid with arsenious acid at* 30°.

$$K = \frac{nK' \times a \times (nc - b + a)}{(b - a)^2} \text{ where } n = 3 \text{ for arsenious acid.}$$

a	b	$3c$	$b-a$	$3c-b+a$	$K \times 10^{-7}$
0·0284	0·2936	0·3463	0·0096	0·2367	2·2
,,	0·3026	0·4929	0·0186	0·4743	1·17
,,	0·3096	0·9861	0·0256	0·9605	1·2

(iv) *Dissociation constant of chromic acid with carbonic acid gas at* 30°.

$$K = \frac{nK \times a \times (nc - b + a)}{(b - a)^2} \text{ where } n = 2 \text{ for carbonic acid.}$$

a	b	$2c$	$b-a$	$2c-b+a$	$K \times 10^{-6}$
0·05714	0·3684	2·000	0·3112	1·688	1·184
,,	0·2601	1·000	0·2029	0·7971	1·32
,,	0·1973	0·500	0·1402	0·3598	1·25
,,	0·1500	0·250	0·0928	0·1572	1·252
,,	0·2541	0·7924	0·1970	0·5954	1·05
,,	0·2460	0·6964	0·1888	0·5076	0·98
,,	0·2637	0·8618	0·2066	0·6552	1·05
,,	0·1760	0·4308	0·1188	0·3120	1·48
,,	0·2143	0·4792	0·1572	0·3220	1·12

(v) *Dissociation constant of boric acid with carbonic acid.*

We have $n = 2$, hence $K' = \frac{2\{K \times a \times (2c - b + a)\}}{(b - a)^2}$

Temp.	a	b	$2c$	$b-a$	$2c-b+a$	$K \times 10^{-9}$
17°	0·08377	0·3470	0·1540 × 2	0·2633	0·0447	3·24
16°	0·06641	0·4213	0·2156 × 2	0·3349	0·0963	4·45
18°	0·08123	0·5288	0·3080 × 2	0·4475	0·1685	4·1

These results are sufficient to prove the validity of our general formula $K = \frac{n'K \times a \times (nc - b + a)}{(b - a)^2}$.

We now proceed to consider our second observation that the dissociation constant increases with dilution. We have already shown that $(b-a)$ is the amount of undissociated acid. In the simple formula $K = \frac{K' \times a \times (c-b+a)}{(b-a)^2}$ we have neglected the ionisation of the acid but this is only partially true. Also as the dilution increases, ionisation increases or the amount of undissociated molecules decreases. Therefore $(b-a)$ decreases with dilution and hence $c-b+a=\{c-(b-a)\}$ increase with dilution. Hence it is quite clear that $K = \frac{K' \times a(c-b+a)}{(b-a)^2}$ should increase with dilution.

The third observation that weaker the acid the lower is the dissociation constant obtained is now to be explained. Let us consider the simple formula,

$$K = \frac{K_1 \times a \times (c-b+a).}{(b-a)^2}$$

The lowering of K means that $(b-a)$ is too large, or the solubility b of the acid in the salt of the acid whose K is required is too great. In case of any acid such as benzoic acid—

$$K_2CrO_4 + C_6H_5 \cdot CO_2H \rightleftarrows C_6H_5 \cdot CO_2K + KHCrO_4 \quad \ldots \quad (i)$$

$$C_6H_5 \cdot CO_2K \; H_2O \rightleftarrows C_6H_5 \cdot CO_2H + KOH \quad \ldots \quad (ii)$$

But the concentration of $C_6H_5 \cdot COO'$ ions must always be $(b-a)$ and if the reaction (ii) occurs simultaneously, then $C_6H_5 \cdot CO_2H$ will be formed or number of $C_6H_5 \cdot COO'$ ions will fall as the acid ionises feebly. Hence more of the acid must dissolve so as to satisfy both the equations. Hence $(b-a)$ increases.

In case of carbonic acid which is weaker than benzoic acid, we have

$$K_2CrO_4 + H_2CO_3 \rightleftarrows KHCrO_4 + KHCO_3 \quad \ldots \quad \ldots \quad (i)$$

$$KHCO_3 + H_2O \rightleftarrows H_2CO_3 + KOH \quad \ldots \quad \ldots \quad (ii)$$

or beeause the reaction (ii) also occurs, therefore as before more of carbon dioxide must dissolve to maintain equilibrium. But the degree of hydrolysis of $C_6H_5 \cdot CO_2K$ is much smaller than that of $KHCO_3$. Hence $(b-a)$ is greater in the case of H_2CO_3, and consequently K is

much lower for H_2CO_3 than with $C_6H_5 \cdot CO_2H$. Thus weaker the acid we are working with, the lower is the dissociation constant obtained.

Thus we have succeeded in giving a theoretical interpretation for the experimental observations.

Summary.

(1) The dissociation constants of hypophosphorous, phosphorous, chromic, hydrofluoric, iodic, titanic, antimonic, boric, vanadic, tungstic and molybdic acids have been determined from solubility measurements of benzoic acid, carbonic acid and arsenious acid in the solution of their sodium or potassium salts.

(2) From the experimental results it has been observed that the formula $K = \frac{K_1 \times a \times (c-b+a)}{(b-a)^2}$ for determining the dissociation constants is specific for monobasic acids; where a=the solubility of the acid used in water, b=the solubility in the salt solution of concentration c, of the acid whose dissociation constant K is required, and K_1 = the dissociation constant of the acid used.

(3) The formula $K_n = \frac{nK(1-k_2)a\{nk_1c-k_3(b-a)\}}{k_4, k_3 (b-a)^2}$ for determining the nth dissociation constant has been deduced taking into consideration the basicity of the acid of which the dissociation constant is required and making due allowance for incomplete ionisation of the various substances used.

(4) It has been shown that the general formula becomes $K_n = \frac{nK \times a[nc-(b-a)]}{(b-a)^2}$ on the assumption that the salts ionise completely and that the weak acids do not ionise. On making further assumption that the acid, whose K is assumed, is monobasic, it reduces to $K_n = \frac{K \times a \times (c-b+a)}{(b-a)^2}$.

(5) It has been observed that the dissociation constant goes on increasing with dilution of the salt solution, and weaker the acid used, the lower is the value of the dissociation constant of the unknown acid. An explanation of these observed facts has been given on the basis of the formula $K_n = \frac{K \times a \times (c-b+a)}{(b-a)^2}$.

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Absorption Spectra of Mixtures of Dilute Solutions of Copper Sulphate and Sodium Sulphite in the Red and the Ultra-violet.

By J. C. Ghosh and Sachindra Nath Chakrabarti.

It is well known that a solution of sodium sulphite undergoes oxidation in the dark in contact with the oxygen of the atmosphere. This oxidation is also accelerated by light. The problem has recently been investigated by Backström (*Medd. k. Vetenskapsad. Nobel Inst.*, 1927, **6**, 16).

Titoff observed long ago that a copper salt, in small traces even, is a powerful positive catalyst for this oxidation in the dark. In view of this observation of Titoff it was felt worthwhile investigating quantitatively the absorption spectra of mixtures of dilute solutions of copper sulphate and sodium sulphite and comparing the values of the extinctions coefficients of the mixtures with the sum of those of the constituents.

Experimental.

The absorptions were measured in the red with the help of a König-Marten spectrophotometer. Lines of quartz mercury-lamp were used in calibrating the instrument.

It was noticed that on mixing a solution of $M/10$-sodium sulphite with $M/500$-copper sulphate which had practically no absorption in the visible, a visible blue colour was developed and that the colour disappeared within a very short interval of its first appearance. Hence, the following precaution was necessary:—Since the mixture is rapidly oxidised in the air, carbon dioxide was passed through the solutions of sodium sulphite and copper sulphate before they were mixed. Carbon dioxide was also passed into the reaction cell for a considerable period of time. Each component of the mixture was separately introduced into the reaction cell and the cell was closed immediately and sealed with soft sealing wax.

The strength of the sodium sulphite in the mixture was at least ten times greater than that of the copper sulphate.

The minimum strength of copper sulphate should be $M/1000$ in the mixture and that of sodium sulphite should not be below $M/100$.

Results.

Size of reaction cell=4 cm. × 4 cm. × 2 cm.
(The cell was placed in the normal position.)

Wave-length of the region investigated=655 $\mu\mu$. Spectrophotometer readings

(1) Zero reading ... 29°
(2) With 10 c.c. of water in the reaction cell ... 28°
(3) With 10 c.c. of $M/500$-$CuSO_4$ soln. in the reaction cell ... 28°

Mixtures.

(A) 5 C. c. of $M/500$-$CuSO_4$ soln. and 5 c.c. of $M/10$-Na_2SO_3 soln..

Date.	Hour.	Readings.
5-4-29.	2-10 P.M.	20° (*a*)
	3-10 ,,	22°
	4-10 ,,	24°
6-4-29.	6 ,,	26° (*a'*)

(*a*) $\log I_o/I_t = 0{\cdot}1462$
(*a*) $\log I_o/I_t = 0{\cdot}0322$

(B) 5 c.c. of $M/500$-$CuSO_4$ soln. and 5 c.c. of $M/20$-Na_2SO_3 soln.
Spectrophotometer readings = 25° (*b*)
(*b*) $\log I_0/I_t = 0{\cdot}0493$.

(C) 5 c.c. of $M/500$-$CuSO_4$ soln. and 5 c.c. of $M/40$-Na_2SO_3 soln.
Spectrophotometer reading=27° (*c*)
(*c*) $\log I_o/I_t = 0{\cdot}0158$.

The following data were obtained in an attempt to find out whether any exaltation in the value of the extinction coefficients of the mixture of copper sulphate and sodium sulphite over the sum of those of the constituents took place in the ultra-violet.

	$\log I_o/I_t$ for	$\log I_o/I_t$ for	$\log I_o/I_t$ for
Wave-length	2961	2770	2600
$M/10$-Na_2SO_3	—	0·1	0·45
$M/500$-$CuSO_4$	0·15	0·2	0·25
Mixture	0·15	0·3	0·7

It will be seen from data given above that there is no exaltation in the value of the extinction coefficients of the mixture.

Discussion.

It will be noticed that there is a very marked increase in the extinction coefficient of the mixtures of the dilute solution of copper sulphate and sodium sulphite in the red region. In fact, $M/500$-copper sulphate appears almost colourless to the eye in layers of 1 cm. thickness whereas on mixing with sodium sulphite solution a very perceptible greenish blue colouration is developed. This increase in absorption coefficient in the red must be due to an unstable intermediate complex formed by the action of copper sulphate with sodium sulphite. This complex decomposes fairly quickly and the greenish blue colour disappears after sometime.

It is curious that the mixtures of copper sulphate and sodium sulphite solutions do not show any exaltation in the extinction coefficient in the ultra-violet between $260\mu\mu$ and $296\mu\mu$. It is very probable that inertness of copper sulphate, so far as the photochemical oxidation of sodium sulphite is concerned, is related to the absence of the exaltation effect in the ultra-violet. It is also probable that the catalytic action of copper sulphate on the 'dark' oxidation of sodium sulphite may find its explanation in the pronounced exaltation of extinction coefficients of the mixtures of these two reactants in the red and infra-red. Further investigation on this subject is in progress.

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The Photochemical Reduction of Ferric Salts by Mandelic, Lactic and Tartaric Acids.

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It is well known that many organic substances reduce ferric salts in presence of light. A large amount of work has already been done on the photochemical oxidation of oxalic acid by ferric salts. But quantitative work on the oxidation of other acids by ferric salts is lacking in thoroughness and accuracy. Reference should be made to the work of Benrath (*Z. physikal. Chem.*, 1910, **74**, 115) Winther and Oxolt-Howe (*Z. wiss. Phot.*, 1914, **14**, 196.) and Bolin (*Z. physikal. Chem.*, 1914, **87**, 490). They all found that the dark reaction had negligible velocity and that the photochemical reactions were zeromolecular. Benrath found that in the case of oxidation of tartaric acid the speed of oxidation is also independent of the concentration of tartaric acid. He did not, however, investigate this point in the case of other acids. This observation of Benrath appears to be inconsistent with a large number of investigations carried out in this laboratory, according to which the inverse of the speed of reaction plotted against the inverse of the concentration of acceptor molecules gave a straight line, $\frac{d\,(1/speed)}{d\,(1/conc.)}$ having always a positive value. A systematic investigation of these reactions was therefore carried out with a view to elucidating the inner mechanism of the process of photochemical oxidation.

It should be noted at the outset that while the oixdation of lactic and mandelic acids consists in the splitting off of carbon dioxide and oxidation of two hydrogen atoms to give respectively acetaldehyde and benzaldehyde, the corresponding oxidation of tartaric acid is a very complicated process. We obtain a host of substances as the reaction products *e.g.*, carbon dioxide, formaldehyde, glyoxal, glyoxalic acid, etc. Some of these reaction products are capable of still further oxidation by ferric salt. Hence the results of experiments on photochemical oxidation of tartaric acid are expected to be different from those observed with lactic and mandelic acids.

Experimental.

The source of light was a 1000 c.p. Pointolite lamp: the strength of current and voltage were maintained constant by means of a regulating resistance. A parallel beam of light was obtained by placing a convex lens at its focal distance from the lamp. The intensity of light was varied by using lenses of different focal lengths. Different spectral regions were isolated by the use of following filters.

Filter A consisted of solutions of Crystal violet and copper sulphate and transmitted a narrow region of spectrum about 448$\mu\mu$.

Filter B consisted of solutions of "Doppel grün" and copper sulphate and transmitted a narrow region of spectrum about 448$\mu\mu$.

Filter C consisted of a plate of Corning glass which transmitted a spectral region between 350$\mu\mu$ and 420$\mu\mu$. Since glass reaction vessels were used the effective radiations had wave-lengths lying between 360$\mu\mu$ and 420$\mu\mu$.

With these filters therefore, small regions of the spectrum round 488$\mu\mu$, 448$\mu\mu$ and 400$\mu\mu$ could be isolated and their photochemical efficiencies studied. The intensity of radiation absorbed was measured by means of a Moll thermopile and Moll galvanometer and compared with the intensity of a standard Hefner. The actual procedure consisted in observing first, the deflections of the galvanometer when light fell on the thermopile after passing through the reacting mixture in the reaction cell, and then observing the deflection when the reaction cell was filled with water only. The difference in deflections is a measure of the light absorbed.

The rectangular reaction cell made of plane parallel glass plates was placed inside a double-jacketted box provided with a glass window to admit light from the lamp. The box was maintained at a constant temperature by circulating water through its annular space from a thermostat by means of a pump. Solutions of ferric salt and organic acids were separately allowed to take up the temperature of the thermostat and were then mixed inside the reaction cell. The rate of reduction of ferric salt was measured by titration. It is essential for accurate work that no extraneous source of light should enter the reaction cell, and the reaction was carried in a perfectly dark room, the only light entering the reaction cell being that obtained from the Pointolite lamp through the glass window.

Effect of Complete Absorption of incident Rays by thin Layers of Reacting Mixture close to Surface of Incidence on Titration Value: The Need of Shaking the Reaction Cell before each Titration.

In the experimental arrangement discribed before, the reaction cell was kept fixed inside a box and the reacting mixture was pippetted out at intervals and titrated, with minimum disturbance of the reaction cell. The results obtained specially when illumination was effected by spectral regions round 448$\mu\mu$ and 400$\mu\mu$ were irregular and disquieting. Table I will bring out the nature of these irregularities.

TABLE I.

Composition of reacting mixture—Mandelic acid=0·1 *M*.
Hydrochloric acid=0·05 *M*.
Ferric chloride=0·025 *M*.

Spectral region—about 448$\mu\mu$.

Time in hours.	Titre values: C.c. of *N*/500-thiosulphate for 2 c.c. of reacting mixture.	Diff. between titration values.
0	25·2	1·6 (between 0 and 1)
1	23·6	2·2 (between 1 and 2)
2	20·4	3·05 (between 2 and 3)
3	18·35	

It appeared as if there was an auto-acceleration. Careful investigation however showed that this irregularity is due to the photochemical reaction taking place in a thin layer close to the surface on which light was incident, and to the slowness of the process of diffusion resulting in the solution being inhomogeneous as regards concentration of ferric chloride. This disturbing influence was found to be much smaller for light round spectral region 488$\mu\mu$, but very much greater for light round spectral region 400$\mu\mu$.

The explanation is obvious. The absorption of light by ferric chloride solutions increases very rapidly as the wave-length diminishes for iargar wave-lengths, *e.g.*, 488$\mu\mu$, the reaction almost takes place in the whole bulk of the liquid mixture, though of course, the speed of reaction in the layers close to the surface of incident light is much larger than in the distant layers. The resulting inhomogeneity

of the mixture as regards ferric salt concentration is not therefore very great. But for wave-lengths round 400$\mu\mu$ a very thin layer of the reacting mixture close to surface of incidence completely absorbs the radiation, and the photochemical reaction is confined within this layer. Since the process of diffusion is slow, the resulting inhomogeneity is very considerable. The titration values recorded in Table II were obtained with this precaution that the reacting mixture was vigorously shaken before each pipetting off.

TABLE II.

Intensity and quality of light, and composition of reacting mixture same as in Table I.

Time in hours.	$N/500$-Thiosulphate for 2 c.c. solution.	Difference.
0	25·2 c.c.	2·3 (between 0 and 1)
1	22·9	2·35 (between 1 and 2)
2	20·55	2·35 (between 2 and 3)

It will be seen that with this precaution, the reaction is found to be zeromolecular, provided the concentration of the oxidisable acid molecule does not undergo considerable variation in the course of experiment. That the above explanation of the irregularity noticed in Table I was correct was further confirmed in the following way. The reaction cell was nearly completely filled with reacting mixture and exposed to light for a definite interval. The cell was withdrawn from the constant temperature box, the contents thoroughly shaken and the amount of total reaction was estimated. The cell was washed, dried, filled up to the same extent with the same reacting mixture, exposed for a longer interval, and the amount of total reaction again determined. The results are given in Table III.

TABLE IIIA.

Composition of reacting mixture—Mandelic acid = 0·5 M.
Ferric chloride = 0·025 M.
Hydrochloric acid = 0·05 M.
Spectral region-about 390$\mu\mu$. Reaction cell = 2·5 × 2·3 × 0·5 cm.

	Total change in terms of $N/500$-thiosulphate.
Exposed for 1 hour	3·4 c.c.
Exposed for 2 hours	6·4 c.c.
Exposed for 3 hours	10·3 c.c.

TABLE IIIB.

Experimental conditions were same as in Table IIIA except that 0·5 *M*-mandelic acid was substituted by 0·5*M*-tartaric acid.

	Total change in terms of $N/500$-thiosulphate.
Exposed for 2 hours	1·85 c.c.
Exposed for 4 hours	3·8 c.c.

TABLE IIIC.

Experimental conditions same as in Table IIIA except that a new reaction cell 3 × 3 × 1 cm. was used.

	Total change in terms of $N/500$-thiosulphate.
Exposed for 1½ hours	8 c.c.
Exposed for 4½ hours	23·8 c.c.

It is quite clear from the above tables, that *with excess of tartaric acid or mandelic acid as acceptor* the photochemical reduction of ferric chloride is zeromolecular even with light of wave-length of about 390$\mu\mu$. A comparison of data in Table IIIA and IIIC will at once bring out the fact that the amount of ferrous salt produced per hour is proportional to the area of the surface on which light was incident.

Depth of Reaction Cell necessary for complete Absorption of Radiations of different Wave-lengths.

Our reactions were carried out mostly with a ferric chloride solution whose concentration was 0·025 *M*. A relationship between the speed of the zeromolecular reaction and the intensity of incident radiation can only be expected to exist only when the whole of the incident radiation is absorbed by the reacting mixture in the cell. For ascertaining the depth of layer necessary for complete absorption of light, rectangular cells, having the same surface area but different depths were used. If the absorption of light were always complete, we would expect that the titre for 2 c.c. of the reaction mixture after exposure for one hour should be inversely as the thicknesses of the cells. The results are recorded in Table IV.

TABLE IV.

Ferric chloride = 0·025*N*. Hydrochloric acid = 0·05N_s

Conc. of mandelic acid.	x/t (1 cm. thick cell)	x/t (1·5 cm. thick cell.)	Ratio of velocities.
	Spectral region = 488$\mu\mu$		
0·5 *M*	3·1	2·35	1·31
0·05 *M*	2·5	1·95	1·28
0·025 *M*	2·1	1·64	1·28
	Spectral region = 448$\mu\mu$		
0·5 *M*	2·57	1·85	1·38
0·2 *M*	2·45	1·78	1·38
0·1 *M*	2·33	1·68	1·39
	Spectral region = 390$\mu\mu$		
0·5 *M*	1·2	0·82	1·48

It is clear from the above tables, that a thickness of 0·5 cm. is sufficient for complete absorption of light in region 390$\mu\mu$ by a 0·025*N*-ferric chloride solution, whereas for wave-lengths between 478$\mu\mu$ and 410$\mu\mu$ for cemplete absorption a thickness of 1 cm. is not sufficient but a thickness of 1·5 cm. is necessary. In the case of light of wave-lengths between 526$\mu\mu$ and 454$\mu\mu$ a thickness of 1·5 cm. is not even sufficient for complete absorption, and for this region it is always essential to measure the intensity of radiation absorbed by actual experiment.

Effect of Hydrochloric Acid on the Speed of Reaction.

It is necessary to add a certain amount of hydrochloric acid to a solution of ferric chloride in order to prevent the hydrolysis of ferric chloride solutions. The effect of adding varying quantities of hydrochloric acid to the reacting mixtures under different conditions of experiment is shown in Table V.

TABLE V.

Spectral region = 488$\mu\mu$.

Ferric chloride = 0·025*M*. Mandelic acid = 0·1*M*.

Hydrochloric acid = 0·0125 *M*.

Time in hours.	$(a-x)$.	x/t ($N/500$-thiosulphate for 2 c.c. of the mixture).
0	25·2	—
1	22·1	3·1 c.c.
2	18·95	3·15
3	15·8	3·15

TABLE VI.

Hydrochloric acid $=0{\cdot}05M$.

Time in hours.	$(a-x)$.	x/t ($N/500$-thiosulphate for 2 c.c. of the mixture).
0	25·2	—
1	22·4	2·8 c.c.
2	19·55	2·8
3	16·8	2·75

For $448\mu\mu$ the values of x/t with $0{\cdot}0125M$-hydrochloric acid were found to be 2·4 and 2·35 respectively.

Hydrochloric acid lowers the extinction coefficient of ferric chloride; necessarily the velocity diminishes as the concentration of the acid increases. By increasing the concentration of hydrochloric acid from $0{\cdot}0125M$ to $0{\cdot}05M$ the diminution in the velocity at $488\mu\mu$ is found to be only about 12 per cent. Hence the concentration of hydrochloric acid ($0{\cdot}05M$) used in these experiments is quite sufficient to prevent completely the disturbing influences due to the dissociation of hydrochloric acid and the hydrolysis of ferric chloride. For $448\mu\mu$ the difference observed is very small which is also to be expected. Even with $0{\cdot}05M$-hydrochloric acid absorption of the incident light is nearly complete at $448\mu\mu$; consequently when the concentration of hydrochloric acid is further reduced there is no material change in the amount of light absorbed and hence the velocity remains practically unaffected.

Hydrochloric acid has thus no effect on the velocity of this reaction except in so far as it diminishes the extinction coefficient for light of longer wave-lengths by ferric chloride solutions.

Influence of Temperature on the Velocity of Reactions.

The experiments were carried out at 25°, 33° and 43°. The temperature coefficient was always found to be unity.

Influence of the Concentration of the Reacting Acids on the Speed of Reaction.

TABLE VII.

Reaction cell=1 cm. thick, 9 sq. cm. area.
Ferric chloride=0·025 *M*. Hydrochloric acid=0·05 *N*.

Conc. of the acid.	x/t in terms of $N/500$-thiosulphate for 2 c.c. of the reaction mixture. 488$\mu\mu$. Energy = 2·22 × 900 ergs.	448$\mu\mu$. Energy absorbed = 1·8 × 900 ergs.	390$\mu\mu$. Energy absorbed = 0·838 × 900 ergs.
Mandelic acid.			
0·5*M*	3·1 c.c. *	2·57 c.c. *	1·2 c.c. *
0·2 *M*	2·98	2·45	—
0·1 *M*	2·8	2·33	1·05
0·05 *M*	2·5	2·15	0·92
0·025 *M*	2·1	1·9	0·75

	Energy absorbed = 1·21 × 900 ergs.
Lactic acid.	
0·5 *M*	0·76
0·1 *M*	0·68
0·05 *M*	0·59

	Energy absorbed = 6·4 × 900 ergs.
Tartaric acid.	
0·5 *M*	4·0
0·1 *M*	4·5
0·05 *M*	4·6
0·025 *M*	4·45

It will be noticed that in the case of tartaric acid the influence of concentration of the acceptor molecule on the velocity of photo-reduction of ferric chloride is negligible, but in the case of lactic acid and mandelic acid, this influence is not inconsiderable. In fact, if the inverse of velocity of photo-reduction is plotted against the inverse of the concentration of the acceptor acid molecules, we get a straight line as will be evident from Fig. 1. Such dependence of the velocity constants on the concentration of acceptor molecules in the case of photochemical reactions has been observed in many cases in

this laboratory. Following Turner (*Phys. Review*, 1924, **23**, 464) it may be concluded that for a constant rate of production of excited ferric ion, the rate of reaction will be given by the equation,

$$V \text{ (velocity)} = C \frac{\tau}{T+\tau} \qquad \ldots \quad (1)$$

where τ is the life-period of the excited molecule, T is the interval on an average between successive collisions of an excited molecule and the acceptor molecule, and C is a constant.

T is further given by $\dfrac{1}{A a^2 p}$

where p is the osmotic pressure of ferric ion expressed in millimetres of mercury, a is the distance between the centres of the excited ferric ion and acceptor molecule on collision, and

$$A = 2666{\cdot}6 \sqrt{\frac{2\pi N}{K\theta} \cdot \frac{m+m_1}{m m_1}}$$

where $N = 6{\cdot}1 \times 10^{23}$, $K = 1{\cdot}371 \times 10^{16}$, θ = absolute temperature, m = molecular weight of ferric ion and m_1 = molecular weight of the organic acid.

Equation (1) becomes $C \left[\dfrac{1}{1 + \dfrac{1}{A a^2 p \tau}} \right] = V$

$$\text{or} \quad \frac{1}{V} = \frac{1}{C} + \frac{1}{C} \cdot \frac{1}{A a^2 \tau} \cdot \frac{1}{p} \qquad \ldots \quad (2)$$

Hence $1/V$ plotted against $1/p$ should be a straight line which has been actually found to be the case.

Life-period of excited Ferric Ion.

Equation (2) enables us to calculate easily the life-period of an excited ferric ion. Assuming van't Hoff's equation, p the osmotic pressure in mm. of mercury can be easily calculated from the molar concentration of ferric salt. The slope of the curves is given by

$$\frac{1}{C} \cdot \frac{1}{A a^2 \tau}$$

and the intercept on the $1/V$ axis for $1/p=0$ or $p=\infty$ is given by $1/C$.

$$\text{Therefore, } Aa^2\tau=\frac{\text{Intercept}}{\text{Slope}} \quad \text{or} \quad \tau=\frac{\text{Intercept}}{\text{Slope}}\cdot\frac{1}{Aa^2}.$$

Assuming $a=3\times10^{-8}$cm., we obtain the values of τ given in Table VIII for excited states of ferric ion.

TABLE VIII.

Wave-length of exciting radiation.	Nature of acceptor molecules.	τ
488$\mu\mu$	Mandelic acid	$1\cdot4\times10^{-9}$
448$\mu\mu$	,,	$1\cdot4\times10^{-9}$
390$\mu\mu$	,,	$1\cdot05\times10^{-9}$
448$\mu\mu$	Lactic acid	$1\cdot1\times10^{-9}$

It will be noticed that the life periods are of the same order of magnitude ; a for collision between ferric ion and lactic acid and mandelic acid is taken to be identical. It is unmistakable that the higher the value of the quantum absorbed the smaller is the life-period of excitation.

In the case of tartaric acid, the reaction is complicated by the fact that the immediate product of photo-oxidation of tartaric acid is in a position to react with ferric salts under the influence of light. Here we are really dealing with a set of consecutive reactions which marks the peculiarities noted in the case of lactic acid and mandelic acid.

Photochemical Efficiency.

The reaction is characterised by great simplicity. The velocity constant is zeromolecular and is not affected by changes of temperature. Hence Einstein's law is expected to hold good. The following table gives the quantum efficiency of the reactions under various experimental conditions. A typical method of calculation is given below :—

Mandelic acid $=0\cdot5M$. Ferric chloride $=0\cdot025\ N$.

Mean wave-length $=488\mu\mu$. Energy absorbed $=2\cdot22\times900$ ergs.

The reaction cell is 1 cm. thick, and 9 sq. cm. area.

(*Vide* Table VII data marked with asterisk.)

The number of quanta absorbed=

$$\frac{2{\cdot}22 \times 900 \times 488 \times 10^{-7} \times 9}{6{\cdot}55 \times 10^{-27} \times 3 \times 10^{10}} = 4{\cdot}4658 \times 10^{14}.$$

Total number of molecules transformed

$$= \frac{9 \times 3{\cdot}1 \times 6{\cdot}1 \times 10^{23}}{2 \times 1000 \times 500 \times 60 \times 60} = 4{\cdot}7277 \times 10^{14}.$$

$$\frac{\text{No. of mols.}}{\text{No. of quanta}} = \frac{4{\cdot}728 \times 10^{14}}{4{\cdot}466 \times 10^{14}} = 1{\cdot}06$$

Quantum Efficiency.

TABLE IX.

	488$\mu\mu$.	448$\mu\mu$.	390$\mu\mu$.
Mandelic acid	1·06 mols.	1·18 mols.	1·36 mols.
Tartaric acid	0·49 ,,	0·52 ,,	0·8 ,,
Lactic acid	0·42 ,,	0·52 ,,	0·8 ,,

It will be seen from the above table that in the case of mandelic acid the quantum efficiency is 1 at 488$\mu\mu$ but becomes nearly 1·4 at 390$\mu\mu$. In the case of tartaric acid and lactic acid the number of molecules transformed per quantum of energy absorbed is nearly 0·5 at 488$\mu\mu$ but goes on increasing as the frequency increases and becomes 0·8 at 390$\mu\mu$.

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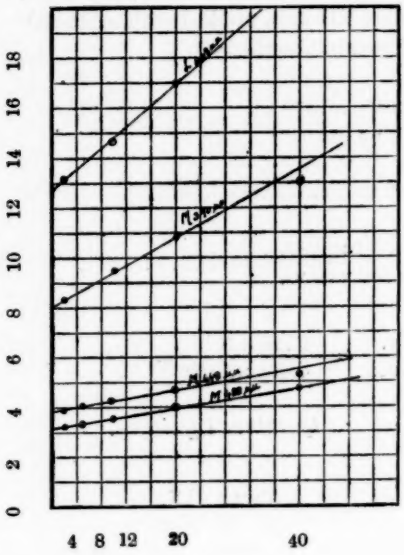

Fig. 1.

The Chemical Examination of the Oil from the Seeds *Butea Frondosa*, Roxb.

By M. C. Tummin Katti and B. L. Manjunath.

The seeds of *Butea Frondosa* are used in Ayurvedic medicine as an anthelmintic drug. (Nadkarni, "The Indian Meteria Medica," 1927, p. 135). Since very little work has been done on the fixed oil in them, the following investigation was undertaken. The observations of Weber and Heckel that the oil formed 18% of the seeds (Wehmer, "Die Pflanzenstoffe," pp. 366, 804) were confirmed. As it was not possible to press out the oil even after steaming the crushed seeds, it was extracted by means of light petroleum (b.p. 50-80°).

Table I.

Physical and Chemical Constants of the Oil.

Specific gravity	... 0·8983 at 25°/25°
Refractive index	... 1·4650 at 25°
Solidifying point	... 15°
Saponification value	... 178
Iodine value (Hanus)	... 67·2
Acetyl ,,	... 23·6
Acid ,,	... 18·1
Reichert-Meisel value	. 0·5
Hehner ,,	... 88·6
Unsaponifiable matter	... 2·3%

Total fatty acids.

Mean molecular weight	... 303·7
Iodine value (Hanus)	... 64·6
Saturated acids (Twitchell's method)	... 35·9%
Unsaturated acids (,, ,,)	... 64·3%

The oil was saponified by alcoholic potash and the resulting soap was dried on paper-pulp and extracted with ether to separate unsaponifiable matter. The soap was then dissolved in water and the fatty acids liberated by the addition of excess of mineral acid. The separation of saturated and unsaturated acids was effected by Twitchell's method (*Ind. Eng. Chem.*, 1921, **13**, 806). The unsaturated acids were converted into their methyl esters which were fractionally distilled under reduced pressure.

TABLE II.

(177 gm. of the esters were distilled.)

Fraction.	Pressure in mm.	Range of temperature.	Distillate in g.	Mean mol. wt. of acids from saponification value.	Iodine value.
I	1·5	Up to 155°	1·47	...	...
II	,,	155-158°	45·87	276·3	115·5
III	0·7	152-153°	22·06	274·5	115·7
IV	0·5	153-154°	21·76	275·6	115·4
V	1·2	154-156°	37·62	282·0	121·1
VI	,,	156-160°	18 90	282·7	118·5
VII	1·5	160-170°	4·76	265·8	106·0
VIII	,,	170-190°	3·51	258·6	89·0
IX	,,	192-206°	4·46	246·0	78·7

The higher fractions showed that with the decreased molecular weights of the acids, the iodine values also decreased considerably. They probably consisted of decomposition products and were rejected. The acids were liberated from the lower fractions. A portion of the mixed acids was treated with bromine according to the method of Eibner and Muggenthaler (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th edition, Vol. I, 585). No ether insoluble additive compound was formed, indicating the absence of linolinic acid. Among the products obtained was isolated tetrabromostearic acid (m.p. 113-114°), which pointed to the presence of linolic acid. On oxidising the acids by cold alkaline permanganate solution, dihydroxystearic acid (m.p. 128-130·5°, mol. wt. 315) and tetrahydroxystearic

acid (m.p. 145-162°*, mol. wt. 349) were formed. The former established the presence of oleic acid and the latter confirmed that of linolic acid.

The saturated acids proved to be of far greater interest. The acids on separation (iodine value, 1·2) were converted into their methyl esters which were subjected to fractional distillation under diminished pressure.

TABLE III.

(243 g. of the esters were distilled.)

Fraction.	Pressure in mm.	Range of temperature.	Distillate in g.	Mean mol. wt. of acids from saponification value.	Acids isolated.
I	2·5	Up to 160°	1·6	281·1	A
II	1·5	160-161°	61·0	270·6	A
III	,,	161-165°	24·8	269·3	A
IV	,,	165-172°	26·0	273·0	A, C and D
V	2·5	185-190°**	20·7	291·0	A, B and C
VI	,,	190-197°	24·0	308·3	B and C
VII	2·0	197-205°	25·2	331·4	B, C and D
VIII	,,	205-212°	36·7	343·9	D
IX	,,	212-222°	19·3	355·4	D and E
X	Residue		1·5	373·0	F

Acid fractions.	M.p.	Mean mol. wt.
A	55-56°	270
B	61-62°	303 (9 g.)
C	75-76°	344 (8 g.)
D	74·5-75·5°	353 (30 g.)
E	77-79°	368 (8 g.)
F	77·5-79°	383 (1 g.)

* It is interesting to note that the tetrahydroxystearic acid obtained melted over a wide range. On melting, the substance solidified at 144° and remelted sharply at 162°. Repeated recrystallisations from various solvents including water did not alter this characteristic of the acid, which is probably a mixture of several isomers.

** 3-4 C.c. of the distillate were collected between 172° and 185°.

The acid from the lower fractions (A) melted at 55-56° (mol. wt. 270). Owing to the fact that successive recrystallisations from various solvents did not alter either its m. p. or M. W. it appeared to be an isomer of margaric acid (m.p. 59·5°, Krafft, *Ber.*, 1879, **12**, 1673). In order to establish its homogeniety fractional precipitation of the magnesium salt (Heintz, *J. pr. Chem.*, 1855, *i* **66**, 3) was also tried but no separation was effected. However, quite fortuitiously, during one of the crystallisations from alcohol a small amount of material separated out melting at 57-58·5° (mol. wt. 266·4). The whole of the acid was converted into its methyl ester, which was then carefully fractionated under diminished pressure. The lower fractions thus obtained gave pure palmitic acid (m.p. 61-62·5°, mol. wt. 256·4). But it was not possible to obtain any information as to the nature of the higher acid present in the mixture. The acids from the higher ester fractions of (A) had indefinite melting points and their mol. wts. ranged from 290 to 324.

During this work no trace of stearic acid was obtained although the mol. wt. of acid fraction (A) corresponded to that of an equimolecular mixture of palmitic and stearic acids. In this connection it is interesting to note that Katti and Puntambaker (unpublished work), while working on the saturated acids from the oil contained in the seeds of *Caesalpina bonducella*, obtained both palmitic and stearic acids, and another acid (m.p. 55-56°, mol. wt. 270) similar to the one under discussion from different fractions of the methyl esters of the total fatty acids. Their last acid was in all probability a mixture of the first two. In the present case, however, owing to the absence of any trace of stearic acid, it is to be deduced that the higher acid in the mixture is presumably one of the higher acids in the mixed fatty acids.

The next acid fraction isolated (B) had a constant melting point of 60-61° (mol. wt. 303). This was obviously a mixture and was proved to be such by the fractional distillation of its methyl ester. Although it was not possible to isolate any definite acid, the melting points and the mol. wts. of the acids * from the different fractions led to the above conclusion.

* Acids from fraction ...	I	II	III
M.p.	61-62°	62-63°	72·5-74°
Mol. wt.	300·9	315·4	345·2

There was obtained another acid fraction of a similar character (C) (m.p. 75-76°, mol. wt. 343), the methyl ester of which on fractional distillation was divided into two fractions. From the first was obtained an acid melting at 77-78° (mol. wt. 351·5). The second also gave an acid which had the same mol. wt., but the melting point was slightly lower (75-76°). No lower acid could be identified.

The acid fraction that proved very interesting was the one which had a constant melting point of 74·5-75·5° (mol. wt. 353). Holde, Bleyberg and Rabinowitsch (*Ber.*, 1929, **62**, 177) isolated a similar substance from the higher acids of the peanut oil (m.p. 73·5-75°, mol. wt. 354). The molecular weight corresponded to that of an equimolecular mixture of behenic and lignoceric acids. These latter acids also were isolated by them from the same source. Thus there is a strong possibility of their acid being a mixture. In the present case, however, although lignoceric acid was isolated from the IXth fraction of the esters, no indication of the occurrence of behenic acid was found. Consequently more detailed work was called for in order to establish the nature of this acid fraction (D).

As in other cases the methyl esters were prepared and fractionally distilled under reduced pressure.

TABLE IV.

(30 g. of the esters were taken. The pressure was less than one mm. throughout the distillation).

No. of fraction.	Range of temperature.		M.p. of acids isolated.	Mol. wt.
I	220-225°	*i*	77-78°	354·0
		ii	,,	345·6 (from mother-liquors of *i*)
II	225-227°	*i*	77-77·6°	352·0
		ii	77-78·3°	347·8 (from mother-liquors of *i*)
III	227-231°	*i*	75-76·5°	353·5
IV	Above 231°	*i*	75-76·5°	367·3 ("crude lignoceric acid")
		ii	75·5-77·2°	355·2 (from mother-liquors of *i*)

The results proved inconclusive. Higher melting acids (77-78°) were obtained from the first two ester fractions. The mother-liquors of these gave about a gram of substance melting at 77-78° (mol.

wt. 345·6). It may be recalled that the higher melting substance of mol. wt. 354 was also obtained from the acid fraction (C) The highest ester fraction, however, gave a small amount of " crude lignoceric acid " (m.p. 75-76·5°, mol. wt. 367·3).*

The results can be interpreted thus: The original acid was " crude tricosoic acid " and that the acid when pure melted at 77-78°. Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 921) synthesised *n*-tricosoic acid and found that it melted at 80-81°. The acid now described might be an isomer. The lower m.p. of the acid fraction (D) is due to the presence of small amounts of a lower acid and lignoceric acid. It is also possible that the acid is a mixture which cannot be definitely separated into its constituents by the process adopted.

In order to obtain more definite information, fractional precipitation of lithium salts (Holde and Godbole, *Ber.*, 1926, **59**, 36) was also attempted.

TABLE V.

No. of fraction.	M. p.	Mol. wt.
I	74-76°	353·6
II	74-75°	354·2
III	74-76°	353·8
IV	,,	353·9

For this purpose the higher melting acid fraction (77-78°) was used. Four distinct fractions of the lithium salts were obtained. On liberating the acids from these, the m.p. was found to have been unaccountably lowered (74-76°) and the mol. wt. remained the same (354). This indicated that no separation had been effected. However, the results cannot be regarded as establishing the identity of the substance, since Holde and others (*loc. cit.*) were able to isolate a small amount of a higher acid from what appeared to be pentacosoic

* Lignoceric acid obtained by Heiduschka and Pyoriki (*Pharm. Zentr.*, 1925, **66**, 1) from the peanut oil melted at 77·5°, even after repeated crystallisations from alcohol. From such an acid Holde and Godbole (*loc. cit.*) were able to isolate pure ignoceric acid (m p. 80-81°). Similarly Holde and others (*loc. cit.*) obtained *n*-behenic acid in a pure state (m.p. 79·2-80·1°) from " crude behenic acid " (m.p. 75·6-76·2°, mol. wt. 340). They consider that the depression of the melting point in these cases is due to the presence of a higher acid in quantities too small to be detected by molecular weight determinations.

acid according to this method. Distillation of the free acid in high vacuo (Holde and others, *loc. cit.*) is expected to lead to more definite conclusions.

From the IXth ester fraction lignoceric acid (m.p. 77-79°, mol. wt. 368) was isolated.

The residue in the distillation flask, on saponification and purification gave about a gram of an acid fraction (F) melting at 77·5-79° (mol. wt. 383). Holde and others (*loc. cit.*) obtained a similar acid (m.p. 78·3-78·8°) from the pea-nut oil; but as has already been mentioned, they isolated from this a small amount of material which approximated to hexacosoic acid. Consequently that the present acid fraction represents a definite chemical entity seems questionable.

In this connection another interesting observation might be recorded. When a mixed melting point of acid fraction (F) with lignoceric acid was taken, no change was observed. This fact goes to indicate that in the case of the higher fatty acids the melting point by itself is not an accurate criterion of purity.

From the unsaponifiable matter a phytosterol (m.p. 133-134°) was isolated. The acetyl derivative of this substance melted at 125-126.° It was evidently sitosterol. The residue left after treatment with digitonin had an oily consistency and it was not possible to isolate any other definite compound.

Thus during this investigation the following compounds were isolated from the oil:

Among unsaturated acids	...	Oleic and linolic acids only.
,, saturated acids	...	Palmitic and lignoceric acids, and acids fractions of mol. wt. 354 and 383.
From unsaponifiable matter	...	Sitosterol.

A more detailed study of the higher acids will form the subject of another communication.

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Mercuration of Coumarins.

By Rajendra Nath Sen and Duhkhaharan Chakravarti.

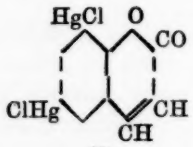
It appears that no attempt has hitherto been made to introduce mercury into coumarins, although mercury derivatives of almost all typical organic compounds have previously been prepared (see Whitmore, "Organic Compounds of Mercury," American Chemical Society Monograph). The present paper deals with the mercurated coumarins.

The most effective reagent previously employed in the mercuration of organic compounds was mercuric acetate and in some cases also mercuric chloride; but these reagents failed to mercurate coumarin in aqueous, alcoholic or acetic acid solution. When, however, the lactonic ring in the coumarin molecule is broken up and the masked hydroxyl group is brought to prominence, mercuration readily takes place either with (*a*) yellow mercuric oxide or with (*b*) mercuric acetate.

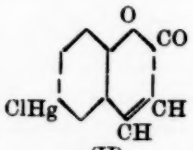
(a) *Mercuration with Yellow Mercuric Oxide.*

Monochloro- and dichloro-mercuricoumarins have been obtained in satisfactory yields by boiling a very dilute alkaline solution of coumarin with yellow mercuric oxide for three to four hours and then acidifying with dilute hydrochloric acid in the cold in the same way as was done by White (*J. Amer. Chem. Soc.*, 1920, **42**, 2355) for mercurating the phthaleins. That the lactone ring with the ethylene linking remains unaffected is established by the observations (1) that their behaviour towards sodium carbonate and bicarbonate is exactly similar to coumarin itself, and (2) that cinnamic acid is not mercurated when similarly treated. These products are soluble in caustic alkalis and the original compounds are reprecipitated by dilute hydrochloric acid in the cold. It is therefore evident that the mercury enters the benzene nucleus, as in the case of phenol. (Dimroth, *Ber.*, 1898, **31**, 2154) in the *ortho* and *para* positions to the hydroxyl group so that the dimercury derivative is 6:8-dichloromercuricoumarin (I) and the mono-mercury derivative is probably 6-chloromercuricoumarin (II), as it has been generally observed in the case of mono-substituted coumarins that substitution occurs more

readily in the position 6 (*para*) than in the *ortho* position (*cf.* 6-nitrocoumarin, *Ber.*, 1887, **20**, 2110; 6-aldehydocoumarin, *J. Amer. Chem. Soc.*, 1928, **50**, 2428; coumarin-6-sulphonic acid, *J. Indian Chem. Soc.*, 1928, **5**, 433).



(I)



(II)

That mercury does not enter in position 7 is shown by the fact that 4:7-dimethylcoumarin also behaves similarly to coumarin and gives a dimercurichloride when treated in the same manner. It is interesting to observe that when the position 6 is occupied by nagative substituents, no mercury compound is formed but geometrical inversion takes place to *ortho*-coumaric acid derivatives as described in another paper.

When freshly prepared and moist, the mono-mercurichloride of coumarin, unlike the dimercurichloride, is soluble in ammonia, the original compound being reprecipitated by dilute hydrochloric acid in the cold ; but when perfectly dried, its solubility in ammonia disappears, though it readily dissolves in caustic alkalis.

By qualitative tests it is found that the hydroxycoumarins such as β-methylumbelliferone and β-methyldaphnetin are also mercurated by similar treatment with mercuric oxide which undergoes drastic reduction and it is not possible to obtain the products in a sufficiently pure condition for analysis, while 6-aminocoumarin is oxidised by this treatment with mercuric oxide.

(b) *Mercuration with Mercuric Acetate.*

Mercuration of coumarin with mercuric acetate takes place by dissolving coumarin in caustic soda, carefully neutralising the excess of alkali with dilute acetic acid in the cold and then adding mercuric acetate to the solution of the coumarinic acid, when a thick voluminous precipitate is thrown down. This precipitate, when dissolved in cold caustic alkalis and reprecipitated by acetic acid, is found to be a diacetoxymercuric derivative of *o*-coumaric acid and not of coumarin, as is proved by its ready solubility in sodium bicarbonate solution with effervescence. When it is boiled with a large volume

of moderately dilute hydrochloric acid, a quantitative yield of *o*-coumaric acid melting at 207—209° is obtained. The identical diacetoxymercuri-*o*-coumaric acid is also obtained when *o*-coumaric acid is treated with yellow mercuric oxide in the manner already described. It is interesting to note that similar inversion with the help of mercuric acetate has been observed in other cases also described in another paper.

By similar treatment with mercuric acetate, the hydroxycoumarins such as β-methylumbelliferone and β-methyldaphnetin, are easily mercurated, diacetoxymercuri-derivatives being obtained, which are insoluble in sodium carbonate or bicarbonate solution. The compound from β-methylumbelliferone readily dissolves in cold caustic alkalis and is precipitated unchanged by dilute acetic acid which shows that the mercury atoms have entered the benzene nucleus to form 7-hydroxy-4-methyl-6:8-diacetoxymercuricoumarins. The compound from β-methyldaphnetin on the other hand is readily decomposed even by cold caustic alkalis, a greyish precipitate of mercury oxides containing metallic mercury being formed, and the product obtained by the addition of acetic acid to the filtrate is free from mercury ; hence it is inferred that, in this case, the mercury atoms are attached to the oxygen of the hydroxyl groups as was also observed by Neogi and Chatterjee in the case of certain phenols and phenol-ethers (*J. Indian Chem. Soc.*, 1928, **5**, 221).

When 6-aminocoumarin in dilute acetic acid solution is warmed to 60-70° with an aqueous solution of mercuric acetate for a few minutes, a crystalline acetoxy mercuric derivative is thrown down. This compound is insoluble in acids and does not respond to the diazo test, which proves the absence of a free amino-group; hence it is evident that the mercury atom replaces the hydrogen in the amino-group and not in the benzene nucleus. This view is further supported by the fact that the beautiful colour of 6-aminocoumarin is completely destroyed as in the case of other derivatives of aminocoumarin in which the hydrogen of the amino-group is replaced by different groups (*cf.* Morgan and Micklethwait, *J. Chem. Soc.*, 1904, **85**, 1230). Such *N*-mercuri-derivatives were also obtained from aromatic amines with mercuric chloride in the presence of sodium bicarbonate by Neogi and Chatterjee (*loc. cit.*).

All the mercury derivatives of coumarin (including those which are freely soluble in ammonia when moist but become insoluble when dry) acquire more or less deep colour (yellow to green when treated

with ammonia in the powdered condition, and these coloured products are all found by qualitative tests to contain nitrogen. It has also been noted that these mercury derivatives are readily soluble in pyridin and the original substances are not precipitated by pouring the pyridin solution into water; in the case of dichloromercuricoumarin, a fine crystalline additive compound with pyridin has been isolated.

The mercury in these compounds has been estimated as mercuric sulphide after oxidation with potassium permanganate and sulphuric acid, strictly following the method described by White (*loc. cit.*).

Experimental.

6-*Chloromercuricoumarin.*—A solution of coumarin (10 g.) in 4 per cent. caustic soda solution (200 c.c.) is diluted with water (500 c.c.) and the solution is boiled with finely powdered yellow mercuric oxide (15 g.) for three to four hours. The yellow solution soon assumes a red colour and the yellow colour of the mercuric oxide changes to grey. The cold solution is then filtered and left in a tall cylinder overnight, when grey precipitates collect at the bottom. The supernatant solution is carefully decanted off, filtered two or three times through an ordinary filter paper and carefully acidified in the cold with dilute hydrochloric acid, when a thick voluminous (slightly reddish) precipitate is thrown down. The precipitate is filtered off, dissolved in ammonia, the ammoniacal solution is rapidly filtered at the pump and acidified with dilute hydrochloric acid in the cold. The precipitate is filtered off, thoroughly washed with large volumes of cold water and finally with rectified spirit. It is then dried in a vacuum desiccator ; almost colourless heavy powder decomposing at 178° (yield, 80%). It is sparingly soluble in alcohol and acetone and insoluble in most of the organic solvents, dissolves in ammonia when moist, readily dissolves in caustic alkalis with a reddish-yellow colour. (Found: Hg, 51·8, 51·6 ; Cl, 8·8. $C_9H_5O_2ClHg$ requires Hg, 52·55 ; Cl, 9·3 per cent.).

6 : 8-*Dichloromercuricoumarin.*—Coumarin (10 g.) is dissolved in a 4% caustic soda solution (200 c.c.) and the solution, diluted with water (500 c.c.) is boiled (3-4 hours) with finely powdered yellow mercuric oxide (40 g.). The solution is filtered, left overnight in a tall cylinder as in the previous case to remove colloidal impurities and carefully acidified with dilute hydrochloric acid in the cold.

The precipitate is filtered, removed to a beaker and treated with ammonia when the monomercuri-derivative goes into solution and the residue assumes a greenish-blue colour. The precipitate is rapidly filtered at the pump from the ammoniacal solution, pressed and thoroughly washed with cold water. It is then dried in a vacuum desiccator and the finely powdered solid washed with warm alcohol (yield, 70%). It is a colourless heavy powder, decomposing at 207°, very slightly soluble in alcohol and glacial acetic acid and almost insoluble in all other organic solvents; insoluble in ammonia, sodium carbonate and bicarbonate solutions but dissolves in warm caustic alkalis without any decomposition. (Found: Hg, 64·3 ; Cl, 10·82. $C_9H_4O_2Cl_2Hg_2$ requires Hg, 65·04 ; Cl, 11·5 per cent.).

This dichloromercuri-derivative is readily soluble in pyridin and on pouring the pyridin solution into water a *compound* is obtained which can be crystallised from a large volume of boiling alcohol. The crystals, thus obtained, are recrystallised from benzene, when colourless needles are obtained melting at 225°. (Found: Cl, 9·8 ; N, 2·3. $C_9H_4O_2Cl_2Hg_2 \cdot C_5H_5N$ requires Cl, 10·23 ; N, 2·02 per cent.).

4:7-*Dimethyl*-6:8-*dichloromercuricoumarin*.—4:7-Dimethylcoumarin (5 g.) is dissolved in caustic soda solution (10%, 50 c.c.) and the solution, diluted with water (400 c.c.) is boiled (3-4 hours) with yellow mercuric oxide (20 g.). The red solution, thus obtained, is filtered off, left overnight in a tall cylinder and the supernatant solution decanted off, filtered through ordinary filter paper and carefully acidified with dilute hydrochloric acid in the cold, when a curdy thick precipitate is obtained. This is filtered off, and thoroughly washed with cold water. It is then dried in a vacuum desiccator and the powdered solid boiled with alcohol. It is a reddish powder, sparingly soluble in glacial acetic acid and insoluble in other solvents, insoluble in ammonia, sodium carbonate and bicarbonate solutions but soluble in warm caustic alkalis. (Found: Hg, 61·4 ; 61·7. $C_{11}H_8O_2Cl_2Hg_2$ requires Hg, 62·2 per cent.).

3:5-*Diacetoxymercuricoumaric acid*.—Coumarin (5 g.) is dissolved in caustic soda solution (5 g. in 50 c.c.) and the cold alkaline solution is carefully neutralised with dilute acetic acid from a burette using litmus as an indicator. Mercuric acetate (15 g. dissolved in 100 c.c. water) acidified with acetic acid, is then readily added from a burette and the solution stirred, when a voluminous precipitate is

thrown down. The solution is then left for about half an hour and filtered. The precipitate is washed with cold water, dissolved in cold dilute caustic potash solution and precipitated with dilute acetic acid. The precipitate is filtered off, washed with water, dried in a vacuum desiccator and crystallised from dilute acetic acid (yield, 60%). It forms colourless needle-shaped crystals, decomposing at 215°. It is readily soluble in glacial acetic acid, ammonia and cold alkalis and also in sodium bicarbonate with effervescence, sparingly in alcohol. A further quantity of the mercury derivative is also obtained from the filtrate on keeping. (Found: Hg, 58·1, 58·2. $C_{13}H_{12}O_7Hg_2$ requires Hg, 58·8 per cent.).

The diacetoxymercuri-*o*-coumuric acid (10 g.) is boiled with water (300 c.c.) containing 10 c.c. of concentrated hydrochloric acid, when it goes into solution. The solution is filtered hot and the filtrate on cooling gives needle-shaped crystals of *o*-coumaric acid, m.p. 207-209°. This on treatment with sulphuric acid gives coumarin (m.p. 69°).

The identical diacetoxymercuri-*o*-coumaric acid (decomposing at 215°) is also obtained when a solution of *o*-coumaric acid (5 g.) in caustic alkali solution (3 g. in 50 c.c.), diluted with water (400 c.c.) is boiled (3-4 hours) with an excess of yellow mercuric oxide (20 g.). The solution is then filtered and the mercury derivative is precipitated with dilute acetic acid, filtered, washed with water, dried and crystallised from dilute acetic acid. (Found: Hg, 58·4. $C_{13}H_{12}O_7Hg_2$ requires Hg, 58·8 per cent.).

4-Methyl-7-hydroxy-6:8-diacetoxymercuricoumarin.—A cold solution of β-methylumbelliferone (5 g.) in hot caustic soda solution is carefully neutralised with acetic acid and a solution of mercuric acetate (15 g.) is rapidly added before the precipitation of β-methylumbelliferone begins and the solution left for half an hour. The dirty yellow precipitate, thus obtained, is filtered, washed with water and dissolved in cold dilute caustic potash solution and precipitated with dilute acetic acid. It is a dirty brown powder sparingly soluble in glacial acetic acid and alcohol, insoluble in sodium bicarbonate solution but readily dissolves in cold alkalis without any decomposition. (Found: Hg, 56·8, 57·04. $C_{14}H_{12}O_7Hg_2$ requires Hg, 57·8 per cent.).

4-Methyl-7: 8-diacetoxymercurioxycoumarin.—A cold solution of β-methyldaphnetin (5 g.) in hot caustic soda solution is carefully neutralised with acetic acid and an aqueous solution of mercuric acetate (15 g.) is rapidly added before β-methyldaphnetin is precipitated and

the solution left for about half an hour. The brown precipitate is filtered, thoroughly washed with water, acidified with acetic acid and dried in a vacuum desiccator. The powdered solid is washed with boiling alcohol to remove β-methyldaphnetin. The substance is a brown powder, insoluble in all the organic solvents and is readily decomposed by cold sodium carbonate and alkali solutions. (Found: Hg, 55·8. $C_{14}H_{12}O_8Hg_2$ requires Hg, 56·5 per cent.).

6-*Acetoxymercuriaminocoumarin*.—A solution of 6-aminocoumarin (2 g.) in dilute acetic acid is treated with a solution of mercuric acetate (4 g.) in water acidified with acetic acid and the solution heated to 60-70° for two or three minutes, when shining crystals separate. These are filtered off, washed with cold water acidified with acetic acid and crystallised from dilute acetic acid The colourless shining prismatic crystals insoluble in acids, did not respond to diazo-test. (Found: Hg, 48·3 ; N, 3·03 . $C_{11}H_9O_4NHg$ requires Hg, 47·7 ; N, 3·34 per cent.).

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Use of Phenolic Acids in the Detection, Separation and Estimation of Metals. Part IV. Colorimetric Detection of Titanium.

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Use has been made of various organic reagents in studying the colour reactions of most of the rare metals. Regarding the colour reactions of titanium mention may be made of the works of Weller (*Ber.*, 1883, **15**, 2593), Levy (*Compt. rend.*, 1893, **103**, 1075, 1195), Hall and Smith (*J. Chem. Soc.*, 1905, **88**, 830), Fenton (*J. Chem. Soc.*, 1908, **93**, 1064), Muller (*J. Amer. Chem. Soc.*, 1911, **33**, 1506, 1510), Lenher and Crawford (*J. Amer. Chem. Soc.*, 1913, **35**, 138). But with the exception of Weller all have used organic reagents. So far as the phenolic acids are concerned, mention may be made of Muller, and Hall and Smith.

In the present paper the action of tannic, gallic, and resorcylic acids on titanium salt solution followed by the addition of sodium acetate has been studied. It has been found that in concentrated titanium solution (1 c.c. = 0·001 gm. TiO_2), tannic acid produces an orange precipitate, whereas gallic acid produces a red-brown and resorcylic acid a faint yellow colorations. On the addition of sodium acetate to the coloured solutions the respective colours are greatly enhanced changing to deep brown and yellow. In dilute titanium solutions the colour produced with gallic acid and sodium acetate varies from reddish-brown to pale yellow; similarly with resorcylic acid and sodium acetate the colour varies from greenish-yellow to faint greenish-yellow. From the fact that tannic acid in concentrated titanium solution gives rise to precipitation and solutions containing excess of alkali or ammonium salts also become turbid by tannic acid and sodium acetate, and owing to the low sensitiveness of resorcylic acid and sodium acetate (1 part titanium in 83,000 parts), these two acids are not well-suited as reagents for the detection of titanium.

It has been observed that only gallic acid can produce maximum colour-effect in titanium solution provided that the solution is very dilute, or, if concentrated, a large excess of the reagent should be employed (for 1 c.c. solution = 0·0006 g. of Ti, at least 8-10 c.c. of 1% gallic acid are required). In extremely dilute titanium solutions, the colour by gallic acid only differs in shade with that produced by gallic acid and sodium acetate, the former being reddish-yellow and the latter greenish-yellow. The coloration produced by gallic acid (alone or along with sodium acetate) is discharged by the addition of a little dilute mineral or oxalic acid; whereas an excess of acetic acid is required for the same. Thus it is safe in every case to add sodium acetate after the addition of gallic acid to neutralise the effect of meneral acids. From the observation that, by minimising the colour-effect somewhat of the titanium solution, coloured by gallic acid and sodium acetate, with excess of 6*N*-acetic acid and then again adding sodium or ammonium acetate, the colour intensifies, it is concluded that sodium or ammonium acetate is essential for the maximum colour-effect, when small amount of gallic acid is used. It can be said that when the colour-forming constituents in the solution remain in maximum associated state, then and then only maximum colouration is produced. This association is helped by sodium or ammonium acetate and is retarded by acid. Similarly the maximum production of colour by an excess of gallic acid can be explained, where an excess gallic acid, like the acetate, causes the association of the colour-forming constituents; further addition of gallic acid, like the acetates, increases the colour in the titanium solution, first coloured by excess gallic acid and then faded by acetic acid.

By gallic acid, or by gallic acid and sodium acetate, an absolute amount of 0·000003 g. Ti can be detected by a pale yellow or pale greenish-yellow coloration in a volume not exceeding 4-5 c.c. In other words, the sensitiveness of the colour reaction is 1 part of Ti in 1,000,000 parts, ignoring the volume (which is generally 1 c.c.) of the reagent added. The sensitiveness in comparison with other reagents for titanium is in no way inferior. In this connection it requires to be pointed that in Muller's (*loc. cit.*) colorimetric determination of titanium by salicylic acid, the stated sensitiveness (1 part TiO_2 in 2,000,000 parts solution) cannot be attained. Strictly speaking from the colour in the body of the solution, sensitiveness stands at 1 in 100,000 parts.

The influence of the presence of many metals and salts which are likely to be present along with titanium during its course of detection has been studied. It has been found that with gallic acid, gallic acid and sodium or ammonium acetate, and with gallic acid in concentrated sulphuric acid, titanium can be detected in presence of the metals such as aluminium, beryllium, chromium, ferrous iron, cerium, thorium, yttrium, zirconium, vanadium, uranium, tungsten, molybdenum, manganese, zinc, nickel, cobalt, calcium, strontium, barium, and magnesium. With excess of gallic acid, or with gallic acid and sodium acetate, preserving the sensitiveness stated above, titanium can be detected in the presence of the metals such as aluminium, beryllium, cerium, thorium, yttrium, zirconium, zinc, manganese, calcium, strontium, barium and magnesium. In the cases of aluminium, thorium, zirconium, cerium and yttrium where gallic acid and sodium acetate produces white gelatinous precipitates, it is better to perform blank tests side by side. In presence of vanadium, before adding the reagent, sulphurous acid is added; this enables to detect 0·00003 g. of titanium in 2 c.c. without considering the volume of the reagent used. In this instance the presence of ferric iron, molybdenum and excess of tungsten and niobium interfere as they also give colour reactions with the reagent.

Titanium can be detected in presence of uranium without loss of sensitiveness as stated above. In this case dilute ammonium acetate or a little dilute acetic acid is added after the addition of sodium acetate, as the colour which uranium produces with gallic acid and sodium acetate is discharged by slight acidity (with acetic acid). In these the presence of other colour-forming elements such as molybdenum, tungsten, niobium, etc., interferes.

In detecting titanium in presence of tungsten, "perhydrol" is added before the addition of gallic acid and sodium acetate. Thereby the reddish-violet colouration changes to light violet, characteristic of titanium (evidently due to reduction of tetravalent titanium). This test enables one to detect 0·000012 g. of titanium present in 2 c.c. In this case also, in presence of other colour-forming metals such as molybdenum or iron (ferrous and ferric), the detection fails.

As a solution of alkali or ammonium molybdate with gallic acid and sodium acetate gives the same colour reaction as titanium, the detection of titanium in presence of molybdenum is not possible by this reagent. But by means of gallic acid in concentrated sulphuric acid the detection of titanium in presence of molybdenum has

been made possible and even 0·000003 g. of titanium (in 2 c.c.) can be detected. In this case too the presence of uranium, vanadium, niobium, and ferric iron interferes.

The detection of small amounts of titanium in presence of ferrous iron, which is impossible by gallic acid and sodium acetate, has also been made possible by using syrupy ammonium acetate instead of 5% sodium acetate solution. The ammonium acetate is poured into the bottom of the solution by means of a pipette and at the junction a small yellow layer due to titanium is noticeable over the violet-blue colour due to ferrous iron. In this way 0·000006 g. of titanium in presence of an excess of ferrous iron can be well detected. The presence of molybdenum, niobium and tungsten however interferes.

In presence of chromium (not excess), nickel and cobalt, the salts of which are themselves coloured, the detection of small amount of titanium is possible. In presence of excess of nickel and cobalt salts, the detection of even 0·000006 g. of titanium in 3-4 c.c. can be well done by gallic acid alone or by gallic acid and sodium acetate. It is better to carry a blank test for comparison.

The effects of the presence of alkali, pyrosulphate, phosphate and ammonium salts (fluorides, chlorides and oxalates) have been studied, with the result that the presence of alkali phosphate (irrespective of the amount) has been found to cause a diminution of sensitiveness by half and the presence of an excess of ammonium chloride causes a formation of turbidity in the test solution after a little while on the addition of the reagent. The presence of fluoride abnormally retards the formation of colour-effects; hence in its presence the detection of titanium is not at all suitable. As for the rest, no disturbing effect is observed.

Experimental.

Praparation of Titanium Solution.—The titanium solution is prepared by fusing 0·5 g. of pure TiO_2 with 6 g. of potassium bisulphate; the melt is extracted with warm 5% sulphuric acid. The solution is made up to 500 c.c. with water acidified with sulphuric acid. Hence 1 c.c. of the above solution contains 0·001 g. of TiO_2 or 0·0006 g. Ti. All the experiments are performed with this solution, only the experiments requiring details are given here. In all the experiments a fresh solution of gallic acid (saturated in cold, which is approximately 1%) is always used.

Colour reactions of titanium with gallic acid and sodium acetate.

Experiment.	Titanium solution (Ti).	Reagent.		Remarks.
		Gallic acid (1%)	Sodium acetate 5%.	
1.	0·000006 g. in 1 c.c.	0·5 c.c.	0·5 c.c.	Greenish-yellow coloration in the body of the sol.
2.	0·000003 g. in 1 c.c.	,,	,,	,,
3.	0·0000006 g. in 1 c.c.	,,	,,	Formation of a pale greenish-yellow coloration at the meniscus ; clearly perceptible.
4.	0·0000003 g. 1 in c.c.	,,	,,	,,
5.	0·0000002 g. in 1 c.c.	,,	,,	No colour formation at the meniscus.
6.	0·000001 g. in 5 c.c.	,,	,,	Colour at the meniscus perceptible.
7.	0·000006 g. in 6 c.c.	1 c.c.	1 c.c.	Faint yellow colour in the body of the sol. ; more clear, on being poured in a glazed porcelain basin.
8.	0·000003 g. in 3 c.c.	0·5 c.c. 1 c.c.	0·5 c.c. 1 c.c.	,, ,,

From Expt. No. 8 the sensitiveness is found to be 1 part of titanium in 1,000,000 parts.

In this connection it should be noted that the presence of much free mineral acid in the titanium solution decreases the sensitiveness, for, on great dilution, the acetic acid set free in the reaction is enough to act on the colour.

Colour reaction of titanium with resorcylic acid and sodium acetate.

Expt.	Titanium solution (Ti).	Water.	Reagent.		Total volume of the Ti soln.	Remarks.
			Resorcylic acid (sat. sol.)	Sodium acetate (5%)		
(*a*)	0·00006 g. in 1 c.c.	Nil	2 c.c.	1 c.c.	4 c.c.	Yellow colour having greenish shade.
(*b*)	,,	5 c.c.	,,	,,	9 c.c.	Light yellow colour in the body of the soln.
(*c*)	,,	9 c.c.	,,	,,	13 c.c.	Yellowish colour at the meniscus but faint in the body of the soln.
(*d*)	0·000006 g. in 1 c.c.	—	,,	,,	4 c.c.	Very faint yellow coloration at the meniscus.
(*e*)	0·00012 g. in 1 c.c.	—	1 c.c.	,,	3 c.c.	Faint yellow colour in the body of the solution.
(*f*)	,,	1 c.c.	,,	,,	4 c.c.	Yellowish coloration at the meniscus.

From (*c*) without considering the volume of the reagents used it is seen that 0·00006 g. of Ti in a volume of 10 c. c. can be easily detected from which the sensitiveness stands at 1 in 166,000 parts. But in (*d*) where 0·00006 g. of Ti is present in 1 c.c. (the same as in *c*) the colour is not as intense as in (*c*); this is due to dilution caused by the volume of the reagent (which is in this case 1-400th and in (*c*) is 1-130th) so to get the sensitiveness in (*d*) equal to (*c*) very small volumes of the reagent should be added, (0·5 c. c.) Using 2 c. c. of the reagent as in (*e*) the sensitiveness stands at 1 in 83,000.

Detection of titanium in presence of vanadium.

In mineral acid solution of vanadium, gallic acid first produces a transient pink-violet coloration (characteristic of vanadium) changing to brownish-yellow. On adding sodium acetate the solution becomes deep blue-black and of colloidal nature. But before adding gallic acid and sodium acetate, if sulphurous acid is added to the vanadium solution, a light blue solution is obtained and in presence of this coloration titanium which imparts a greenish yellow colour to the whole solution can be detected. In performing the test the volume of sulphurous acid added should be equal to the volume of the test solution and then 0·5 c.c. gallic acid and 3·4 c.c. 5% sodium acetate should be added for each 0·002 g. of vanadium. Following the above direction 1 c.c. of titanium solution of 1-20th dilution with 1 c.c. of 0·2% vanadium solution can be easily detected from the greenish-yellow colour. Thus 0·00003 g. of titanium is detectable in a volume of 2 c.c. *i.e.*, the sensitiveness is 1 in 67,000. In this the presence of molybdenum, ferric iron and excess of niobium and tungsten interferes as, with gallic acid and sodium, acetate molybdenum, niobium, and tungsten give brown or yellow colorations and ferric iron gives deep blue-black colloidal solution. In detecting titanium in presence of vanadium it is better to perform a similar test with vanadium solution only, side by side for comparison.

Detection of titanium in presence of tungsten.

Gallic acid, or gallic acid and sodium acetate produces a yellow coloration with a solution of sodium tungstate. To this by adding dilute sulphuric acid the colour becomes dark brown (this may serve

as a sensitive test for tungsten) whereas with titanium solution gallic acid and sodium acetate produce a reddish-brown to yellow coloration according to the amount of titanium present. As both titanium and tungsten produce coloration almost of the same nature, it is difficult to identify titanium in presence of tungsten; with large amounts of titanium however, its presence can be detected as by the addition of gallic acid and excess of sodium acetate, a brown coloration will be produced due to the presence of titanium, whereas it is only yellow with a greenish shade in the case of tungsten. When small amounts of titanium are present, the reagent cannot distinguish titanium; but by the behaviour of dilute sulphuric acid on the colored solution, tungsten can be found out but not titanium, as with sulphuric acid the yellow solution becomes brown in the case of tungsten and colourless in the case of titanium.

To detect the presence of small amounts of titanium in tungsten, to the feebly acidic solution at first "perhydrol" is added and then gallic acid and excess of sodium acetate which gives a reddish-violet to light violet coloration with titanium according to its amount and no coloration at all with tungsten. After 2-3 minutes, the appearance of the violet coloration becomes more prominent. The optimum conditions for performing the test are as follows:

1. The solution should not contain much free mineral acid (in that case a large excess of sodium acetate is required, which diminishes the sensitiveness of the reaction).

2. Excess of "perhydrol" should be added (for 2 c c. test solution at least 2 c.c. are added).

3. Gallic acid added should be small (0·5 c.c. for 2 c.c. test solution).

4. Sodium acetate should be added in excess, till the light yellow colour of the solution is discharged.

5. Tungsten should not be present in large excess, as in that case a large excess of sodium acetate is required to make the solution (which is of pale yellow colour) colourless and thus the sensitiveness is much diminished.

Small amounts of vanadium (of the order 0·0004 g.) and niobium, on being treated as above behave like tungsten. Consequenthy titanium can also be detected in their presence. Molybdenum and iron on being thus treated give brown and blue-black colorations respectively and thus interfere with the detection of titanium.

Detection of titanium in presence of molybdenum.

Studying the action of gallic acid in concentrated sulphuric acid on aqueous or dilute acidic solutions of all colour-forming metals such as uranium, titanium, vanadium, niobium, iron (ferrous and ferric), molybdenum and tungsten, it has been found that with the exception of tungsten and ferrous iron, all produce more or less brown colorations. If the reagent is added carefully such that it forms two distinct layers, molybdenum produces a yellow layer at the zone of contact and titanium a violetish-brown layer which becomes more visible after 2-3 minutes. Whereas others also at first form coloured layers, which readily distribute throughout the solution; the colour due to vanadium and ferric iron distributes only in the upper layer and that due to uranium in the lower layer only. It has been found that in their presence the detection of titanium in presence of molybdenum is not possible.

When both titanium and molybdenum are present in a solution, the brown layer due to titanium rests on the yellow layer due to molybdenum. After standing, the brown layer is seen between two yellow layers, thus the colour due to molybdenum slowly distributes in the upper layer. By this test titanium can also be detected in presence of tungsten and ferrous iron. Gallic acid in concentrated sulphuric acid with tungsten produces a white precipitate, turning to yellowish white after sometime. The presence of titanium in tungsten is detected by the formatien of a brown layer below the yellowish-white precipitate probably of tungstic oxide, with a slight colorless gap between the two. The reagent produces practically no coloration with ferrous iron. Further in this connection the action of the reagent on a mixture of tungsten and molybdenum solution has been studied with the result that a yellow layer is obtained below the first formed white precipitate due to tungsten. The precipitate in this case gradually becomes green instead of yellowish and this is evidently due to molybdenum. This test seems to be characteristic of molybdenum, and consequently the presence of molybdenum in tungsten can be easily detected. When a solution contains titanium, tungsten and molybdenum, on the addition of the reagent, at first the brown layer due to titanium over the yellow layer due to molybdenum is noticed and after a longer time, a white turbidity due to tungsten appears, which on standing increases in bulk and becomes green.

In the colour reaction of titanium with gallic acid and sodium acetate, it has been found that the colour produced is proportional to the amount of titanium present in a solution and hence its colorimetric determination seems possible. The work is in progress.

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Synthesis of Lengthened Sulphur Chain Compounds.

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When alcoholic potassium hydrosulphide acts upon trimethylene dibromide (Hagelberg, *Ber.*, 1890, **23**, 1085 ; Austenrieth and Wolff, *Ber.*, 1899, **32**, 1369) the main product of reaction is the mercaptan $SH\cdot(CH_2)_3\cdot SH$ which can be separated from the reaction mixture by steam distillation.

The residue on acidification with dilute sulphuric acid gave an oil which after purification boiled at 180°/40 mm. In view of the interesting by-products obtained by Rây (*J. Chem. Soc.*, 1923, **123**, 134) in the preparation of dithioethylene glycol, we thought it desirable to examine this componnd. The constitution of the compound, from analytical data and chemical properties, appears to be $SH\cdot(CH_2)_3\cdot S\cdot S\cdot(CH_2)_3\cdot SH$, which is probably formed by the partial oxidation of 1 : 3-dithiopropylene glycol.

We attempted to prove the constitution of the compound definitely by synthesis. Our plan was to protect one of the thiol groups of the thioglycol, oxidise the compound and finally remove the protecting groups. Thus :—$RS\cdot(CH_2)_3\cdot SH \longrightarrow RS\cdot(CH_2)_3\cdot S\cdot S\cdot(CH_2)_3\cdot SR \longrightarrow SH\cdot(CH_2)_3\cdot S\cdot S\cdot(CH_2)_3\cdot SH$.

With this object in view, we attempted to acetylate the mercaptan partially by the direct action of acetic anhydride on the mercaptan. The product of the reaction under a variety of conditions was always found to be the disubstituted compound which was obtained in rather poor yield. In presence of pyridine however, the yield increased from 14 % to 88 %. The ester was then hydrolysed by 15% caustic potash solution at the room temperature when the desired mono-ester $AcS\cdot(CH_2)_3\cdot SH$ was obtained. This was oxidised by iodine in ethereal solution to the disulphide and subsequently the acetyl groups were removed by hydrolysis with potassium hydroxide solution on the water-bath. The dimercaptan thus obtained appeared to be identical with the compound isolated from the products of interaction of trimethylene dibromide and potassium hydrosulphide. In this connection, it was found that

dithioethylene glycol by a series of similar reactions, gives the compound $AcS{\cdot}(CH_2)_2{\cdot}S{\cdot}S{\cdot}(CH_2)_2{\cdot}SAc$, which however, could not be made to give the desired mercaptan, $SH{\cdot}(CH_2)_2{\cdot}S{\cdot}S{\cdot}(CH_2)_2{\cdot}SH$.

EXPERIMENTAL.

Hexamethylene Disulphide Dimercaptan, $SH{\cdot}(CH_2)_3{\cdot}S{\cdot}S{\cdot}(CH_2)_3{\cdot}SH$.

202 Gm. of trimethylene dibromide were mixed with 112 gm. of potassium hydroxide (14% in alcohol) which had previously been saturated with sulphuretted hydrogen in the cold (Hagelberg, *Ber.*, 1890, **23**, 1085 ; Austenrieth and Wolff, *Ber.*, 1899, **32**, 1369). The product was distilled in steam. The residue, left after steam distillation, was acidified with dilute sulphuric acid when an oil separated. This was extracted with ether and the ethereal solution was dried over anhydrous sodium sulphate. The ether was then removed and the residue was distilled under reduced pressure when a yellow mobile liquid boiling at 180°/40 mm. was obtained. (Found: C, 33·83 ; H, 6·6 ; S, 57·81 ; SH (by iodine), 1·91 ; M.W. (cryoscopic in benzene) 180; 183. $C_6H_{14}S_4$ requires C, 33·6; H, 6·5 ; S, 59·8 per cent. ; SH, 2.). M.W. 214 ;

Hexamethylene disulphide dimercaptan possesses an unpleasant smell characteristic of mercaptans in general. It boils at 267° at atmospheric pressure with slight decomposition. It forms lead (orange yellow) and mercuric (white) salts with the oxides of the respective metals, like 1:3-dithiopropylene glycol though less readily. It is insoluble in water, sparingly soluble in alcohol, but easily in ether, benzene, acetone, etc. It forms insoluble compounds readily with mercurous nitrite and mercuric chloride.

1:3-*Diacetyl-dithiopropylene glycol*, $CH_3CO{\cdot}S(CH_2)_3{\cdot}S{\cdot}COCH_3$. —A few drops of pyridine were added to a mixture of the mercaptan (1 part) and acetic anhydride (2 parts) when heat developed gradually. The reaction was completed by refluxing the mixture for 6 hours. The end of the reaction was indicated by the reluctance of a test portion to absorb iodine. After cooling, the product was shaken with excess of water several times. The oil was extracted with ether, and the ethereal solution left overnight over anhydrous sodium sulphate. The ether was removed and the residue distilled at

178°/50 mm. (yield, 88%). (Found: C, 43·4 ; H, 6·38 ; S, 31·85 ; M.W. (cryoscopic in benzene), 189. $C_7H_{12}S_2O_2$ requires C, 43·6 ; H, 6·25 ; S, 33·33 per cent.; M. W. 192.)

The substance is a bright lemon-yellow liquid, b. p. 255°, possessing a peculiar ester-like smell. It is insoluble in water but very soluble in the common organic solvents. It decomposes on continued boiling.

Monoacetyl-1 : 3-dithiopropylene glycol, $CH_3CO{\cdot}S{\cdot}(CH_2)_3{\cdot}SH$. —The mercaptan (47 gm.) and potassium hydroxide (31 gm. in 200 c.c. of water) were shaken vigorously in an electric shaker for 18 hours at the room temperature (28°—30°). The solution was then neutralised with hydrochloric acid, and the emulsion thus formed was extracted by means of ether.

The ethereal extract, after dehydration by means of anhydrous sodium sulphate was distilled under reduced pressure, in an atmosphere of carbon dioxide. At about 70° 1 : 3-dithiopropylene glycol which was partly produced in the process of hydrolysis, distilled over. At 115°—116°/40 mm. the mono-acetylated compound distilled over. (Yield 21·8%). (Found: C, 39·87 ; H, 6·60 ; S, 40·49 ; SH (by iodine), 0·9.; M.W. (cryoscopic in benzene), 145 ; 141. $C_5H_{10}OS_2$ requires C, 40·0 ; H, 6·66 ; S, 42·66 per cent.; SH, 1) ; M. W., 150.

Monoacetyl-1 : 3-dithiopropylene glycol is a light yellow liquid having a sweet ester-like smell quite distinct from that of the parent mercaptan. It is insoluble in water, but is miscible in all proportions with common organic solvents. It decolorises iodine, and on long standing gradually decomposes, when smell of 1 : 3-dithiopropylene glycol is evolved. It also readily forms insoluble compounds with mercuric chloride and mercurous nitrite, etc. and gives coloration with lead acetate papers.

Diacetyl derivative of Hexamethylene Disulphide Dimercaptan, $CH_3CO{\cdot}S{\cdot}(CH_2)_3{\cdot}S{\cdot}S{\cdot}(CH_2)_3\,S{\cdot}COCH_3$.

Monoacetyldithiopropylene glycol in ethereal solution was shaken with the gradual addition of solid iodine, at the room temperature, until the coloration of iodine was persistent. The excess of iodine was removed by a little sodium thiosulphate solution. The ethereal solution was then washed several times with water and finally with dilute sodium carbonate solution. After drying the solution and removal of ether, the product was obtained as an oil. (Found: C, 39·91 ; H, 5·82 ; M. W. (cryoscopic

in benzene) 274, 280. $C_{10}H_{18}O_2S_4$ requires C, 40·26 ; H, 6·04 per cent. ; M.W., 298).

The ester is a mobile yellowish liquid possessing a peculiar characteristic odour. It is insoluble in water but soluble in common organic solvents. It decomposes at ordinary atmospheric pressure at a temperature below its b.p.

Hexamethylene Disulphide Dimercaptan, $SH\cdot(CH_2)_3\cdot S\cdot S\cdot(CH_2)_3\cdot SH$.

Diacetyl hexamethylene disulphide dimercaptan was heated with an excess of potassium hydroxide (15% soln.) on the water-bath. The resulting product was then acidified with hydrochloric acid which liberated the mercaptan. This was finally extracted by means of ether and the disulphide dimercaptan was obtained as an oil after removing the ether on the water-bath under reduced pressure. (Found: C, 32·1 ; H, 6·88 ; S, 58·38 ; M. W. (cryoscopic in benzene), 200 ; SH (by iodine), 1·8. $C_6H_{14}S_2$ requires C, 33·6 ; H, 6·5 ; S, 59·8 per cent. ; M. W., 214 ; SH, 2).

The mercaptan thus obtained is a yellow mobile liquid like the by-product obtained in the preparation of 1 : 3-dithiopropylene glycol, and possesses an unpleasant smell characteristic of mercaptans. It boils at 258° at ordinary pressure and forms orange and white insoluble precipitates with oxides of lead and mercury respectively. It is insoluble in water, sparingly soluble in alcohol, but completely miscible with common organic solvents.

Diacetyldithioethylene glycol, $CH_3CO\cdot S\cdot(CH_2)_2S\cdot COCH_3$.—This was obtained in quantitative yield from dithioethylene glycol and acetic anhydride in the way mentioned before. It crystallised from alcohol in the form of white needles, m. p. 60°. It is soluble in most organic solvents. (Found: C, 40·16 ; H, 5·8 ; S, 34·1. $C_6H_{10}O_2S_2$ requires C, 40·45 ; H, 5·61 ; S, 35·94 per cent.).

Monoacetyldithioethylene glycol, $CH_3CO\cdot S(CH_2)_2\cdot SH$.—This was obtained by the hydrolysis of the diacetyl derivative (*cf.* preparation of monoacetyl-1 : 3-dithiopropylene glycol) for 12 hours. The product after purification was obtained as a colourless oil, b. p. 95°-97°/40 mm. (Found: C, 35·59 ; H, 6·12 ; M.W. (cryoscopic in benzene), 130. $C_4H_8S_2O$ requires C, 35·29 ; H, 5·88 per cent.; M.W., 136).

It possesses a peculiar ester-like smell. It is insoluble in water but soluble in common organic solvents. On long standing it gives a smell of dithioethylene glycol. It decolorises iodine, and forms

insoluble compounds with lead oxide, mercuric chloride and mercurous nitrite.

Diacetyl derivative of Tetramethylene Disulphide Dimercaptan, $CH_3CO{\cdot}S(CH_2)_2{\cdot}S{\cdot}S{\cdot}(CH_2)_2{\cdot}S{\cdot}COCH_3$.— This compound was prepared like the corresponding diacetylhexamethylene disulphide dimercaptan, by treatment of the mono-acetylated product ($CH_3CO{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}SH$) with iodine. The pure compound was obtained as a colourless oil. (Found: C, 35·4 ; H, 5·37 ; S, 45·72 ; M. W. (cryoscopic in benzene) 250. $C_8H_{14}O_2S_4$ requires C, 35·55 ; H, 5·19 ; S, 47·4 per cent.; M. W., 270).

The substance when treated with dilute aqueous alkali on the water-bath decomposed completely. On treatment with 15% sodium carbonate solution a yellowish oil, b. p. 180° was obtained. The yield was insufficient for purification, analysis, and further studies.

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Extinction Coefficient of Mixtures of Copper Sulphate with Glucose, Glycerine and Sodium Formate in the Ultra-violet as Experimental Evidence in Favour of the Formation of Unstable Intermediate Compounds. Part IV.

By J. C. Ghosh and Sachindra Nath Chakrabarti.

In a previous paper by Ghosh and Rangacharya (*J. Indian Chem. Soc.*, 1928, **5**, 569) it has been shown that the observed exaltation in values of extinction coefficients when mercuric chloride is mixed with organic acids, can be explained quantitatively on the hypothesis that an intermediate compound is produced by the association of one molecule of mercuric chloride with one molecule of organic acid. The dissociation constants of these intermediate compounds and their extinction coefficients for several wave-lengths in the ultra-violet were calculated according to a method developed in the paper by Ghosh and Mitra (*J. Indian Chem. Soc.*, 1927, **4**, 353).

It is well known that glucose, glycerine and formates undergo photochemical decomposition in presence of alkaline copper sulphates. The general mechanism of the photochemical decomposition is not yet definitely settled and this investigation was also undertaken with the object of finding out if the hypothesis of formation of intermediate compounds preliminary to photo-decomposition is supported by measurements of extinction coefficient of the photo-sensitive mixtures.

The experimental procedure and methods of calculation are identical with those adopted in the previous works.

Copper sulphate was employed in two forms, namely, in Benedict's solution and in Fehling's solution.

In the latter case the experimental data recorded in the tables in this paper can be quantitatively explained on the basis of—

(1) An equilibrium between copper sulphate and glucose, and copper sulphate and glycerine as reactants and the intermediate complex formed by the loose combination of one molecule of each of the reactants.

(2) The assumption of a definite value of molecular extinction coefficients for each wave-length for the intermediate complex so formed.

But in the case of copper sulphate in Benedict's solution it was observed, curiously enough, that while the first assumption was completely borne out by the experimental data at hand, the assumption of a constant value of the molecular extinction coefficient of the intermediate complex for all the wave-lengths had to be made in order to explain quantitatively the experimental results obtained.

Experimental.

The Fehling's solution was made in two parts.

(A) $CuSO_4$, $5H_2O$ (recrystallised) 6·92 gm. in 100 c. c.

(B) 13 Gm. of NaOH + 34·6 gm. of Rochelle salt in 100 c. c.

Mixture of equal volumes of (A) and (B) gave Fehling's solution.

The extinction coefficients were measured with the aid of the rotating sector-photometer of Adam Hilger in conjunction with their quartz spectrograph.

Though the photographic density of the two spectra in juxtaposition can be compared fairly accurately, still the probability of error in the value of extinction coefficients is certainly $\pm 7\%$.

The length of the tube containing the solution under investigation was 2 cm. in all the cases.

Fehling's solution of very small copper sulphate-concentration was used so that the solution showed no visible colour to the eye.

In the following tables,

$$K = \frac{\text{Conc. of intermediate compound}}{\text{Conc. of unchanged copper sulphate} \times \text{Conc. of unchanged organic molecule}}$$

x=Conc. of intermediate compound,

$E_{calc.}$=The calculated value of the extinction coefficient of the mixture assuming a definite value of the molecular extinction coefficient (E_M^{λ}) for each wave-length.

Table I.

$M/2400$-$CuSO_4$ (*Fehling's Sol.*) *and Glucose* (K=100).

$\log I_0/I_t$=Extinction coefficient (E)

x=Cone. of intermediate complex as calculated.

F=Fehling's solution.

(—) indicates that the extinction coefficient is negligibly small.

	log I_0/I, for			
Wave-length ...	3750	3248	3036	$\varepsilon_{calc.}$
$M/2400$ (F), $E_{obs.}$	—	0·15	0·4	
$M/25$-Glucose, $E_{obs.}$	—	—	—	
Mixture, $E_{obs.}$	0·1	0·4	0·75	$0·34 \times 10^{-3}$
$E_{calc.}$	0·1	0·4	0·73	
$M/50$-Glucose, $E_{obs.}$	—	—	—	
Mixture $E_{obs.}$	0·1	0·35	0·7	$0·28 \times 10^{-3}$
$E_{calc.}$	0·09	0·35	0·68	
$M/100$-Glucose, $E_{obs.}$	—	—	—	
Mixture, $E_{obs.}$	0·05	0·3	0·6	$0·21 \times 10^{-3}$
$E_{calc.}$	0·06	0·28	0·61	
$M/250$-Glucose, $E_{obs.}$	—	—	—	
Mixture, $E_{obs.}$	0·05	0·2	0·55	$0·14 \times 10^{-3}$
$E_{calc.}$	0·04	0·22	0·54	

In calculating the values of E for the various mixtures K has been assumed to be 100 in all the cases and E_M (molecular extinction coefficient of the intermediate complex) given the following values for various wave-lengths:—

Wave-length ...	3750	3248	3036
E_M ...	$0·156 \times 10^3$	$0·36 \times 10^3$	$0·504 \times 10^3$

With $M/1200$-copper sulphate in Fehling's solution and varying concentrations of glucose the observed values of extinctions

coefficients for mixtures could be reproduced by assuming $K=200$ and E_M given the following values for various wave-lengths.

Wave-length ...	3750	3440	3248
E_M ...	$0{\cdot}15\times10^{3}$	$0{\cdot}18\times10^{3}$	$0{\cdot}366\times10^{3}$

TABLE II.

M/2400-$CuSO_4$ (*Fehling's sol.*) *and Glycerine* (K=18).

	log I_0/I_t for	log I_0/I_t for	
Wave-length	3248	3036	$x_{calc.}$
M/2400-(F), $E_{obs.}$	0·15	0·4	
M/5-Glycerine, $E_{obs.}$	—	—	
Mixture, $E_{obs.}$	0·4	0·75	$0{\cdot}325\times10^{-3}$
$E_{calc.}$	0·39	0·75	
M/10-Glycerine, $E_{obs.}$	—	—	
Mixture, $E_{obs.}$	0·35	0·7	$0{\cdot}265\times10^{-3}$
$E_{calc.}$	0·35	0·69	
M/20-Glycerine, $E_{obs.}$	—	—	
Mixture, $E_{obs.}$	0·3	0·6	$0{\cdot}195\times10^{-3}$
$E_{calc.}$	0·31	0·61	
M/40-Glycerine, $E_{obs.}$	—	—	
Mixture, $E_{obs.}$	0·25	0·55	$0{\cdot}125\times10^{-3}$
$E_{calc.}$	0·25	0·54	
M/100-Glycerine, E_{obs}	—	—	
Mixture, $E_{obs.}$	0·2	0·45	$0{\cdot}062\times10^{-3}$
$E_{calc.}$	0·19	0·47	

In obtaining the values of $E_{calc.}$ K has been assumed to be 18 in all the cases and the following values of E_M given for various wave-lengths.

Wave-length ...	3248	3036
E_M ...	39×10^{3}	$0{\cdot}56\times10^{3}$

With $M/1200$ concentration of copper sulphate in Fehling's solution and varying concentrations of glycerine extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by assuming $K=18$, and E_M as given below.

Wave-length ...	3308	3164
E_M ...	$0{\cdot}19\times10^{3}$	$0{\cdot}29\times10^{3}$

The Benedict's solution consisted of: –

Anhydrous sodium carbonate	= 9 gm.
,, copper sulphate	= 1 gm.
Sodium citrate	= 17 gm.
Water	= 73 gm.
	100 gm.

A dilute solution of copper sulphate was used.

TABLE III.

M/16·000-$CuSO_4$ (*Benedict's solution*) *and Glucose* (K=100).

	$\log I_0/I$, for			
Wave-length	2507	2370	2266	x calc.
$M/16\,000$-$CuSO_4$, $E_{obs.}$	0·15	0·25	0·3	
$M/25$-Glucose, $E_{obs.}$	—	—	—	
Mixture, $E_{obs.}$	0·4	0·5	0·55	$0{\cdot}050\times10^{-3}$
$E_{calc.}$	0·4	0·49	0·55	
$M/50$-Glucose, $E_{obs.}$	—	—	—	
Mixture, $E_{obs.}$	0·35	0·45	0·5	$0{\cdot}041\times10^{-3}$
$E_{calc.}$	0·35	0·45	0·5	
$M/100$-Glucose, $E_{obs.}$	—	—	—	
Mixture, $E_{obs.}$	0·3	0·4	0·45	$0{\cdot}031\times10^{-3}$
$E_{calc.}$	0·30	0·4	0·45	
$M/200$-Glucose, $E_{obs.}$	—	—	—	
Mixture, $E_{obs.}$	0·25	0·35	0·4	$0{\cdot}021\times10^{-3}$
$E_{calc.}$	0·24	0·3	0·4	

In obtaining the values of $E_{calc.}$ K has been assumed to be 100 in all the cases and following constant value of E_M given.

Wave-length	...	2507	2370	2266
E_M	...	$2{\cdot}4 \times 10^3$	$2{\cdot}4 \times 10^3$	$2{\cdot}4 \times 10^3$

With M/8000 concentration of copper sulphate in Benedict's solution and varying concentrations of glucose extinction coefficients could be measured for higher wave-lengths and the observed values reproduced by assuming $K=100$ and E_M as given below.

Wave-length	...	2270	2507	2370
E_M	...	$2{\cdot}4 \times 10^3$	$2{\cdot}4 \times 10^3$	$2{\cdot}4 \times 10^3$

TABLE IV.

M/16000-$CuSO_4$ (*Benedict's solution*) *and Sodium Formate* (K=10).

	log I_0/I, for				
Wave-length	2770	2667	2400	2370	x calc.
M/16000-$CuSO_4$, $E_{obs.}$	0·1	0·15	0·2	0·25	
M/5-Sodium formate, $E_{obs.}$	—	—	0·15	0·2	
Mixture, $E_{obs.}$	0·3	0·35	0·55	0·65	$0{\cdot}041 \times 10^{-3}$
$E_{calc.}$	0·3	0·35	0·55	0·65	
M/10-Sodium formate, $E_{obs.}$	—	—	0·1	0·15	
Mixture, $E_{obs.}$	0·25	0·3	0·45	0·55	$0{\cdot}031 \times 10^{-3}$
$E_{calc.}$	0·25	0·30	0·44	0·55	
M/20-Sodium formate, $E_{obs.}$	—	—	0·05	0·1	
Mixture, $E_{obs.}$	0·2	0·25	0·35	0·45	$0{\cdot}021 \times 10^{-3}$
$E_{calc.}$	0·2	0·25	0·34	0·44	
M/50-Sodium formate, $E_{obs.}$	—	—	—	0·05	
Mixture, $E_{obs.}$	0·15	0·2	0·25	0·35	$0{\cdot}01 \times 10^{-3}$
$E_{calc.}$	0·15	0·2	0·25	0·35	

In obtaining the values of $E_{calc.}$ K has been assumed to be 10 in all the cases and the following constant values of E_M given.

Wave-length	...	2770	2667	2400	2370
E_M	...	$2{\cdot}39 \times 10^3$	$2{\cdot}39 \times 10^3$	$2{\cdot}39 \times 10^3$	$2{\cdot}39 \times 10^3$

With $M/8000$-concentration of copper sulphate in the Benedict's solution and varying concentrations of sodium formate extinction coefficients for mixtures could be measured and the observed values reproduced by assuming $K = 10$ and $E_M = 2{\cdot}4 \times 10^3$ for all wave-lengths.

Wave-length	...	2667	2469	2400	2370
E_M	...	$2{\cdot}4 \times 10^3$	$2{\cdot}4 \times 10^3$	$2{\cdot}4 \times 10^3$	$2{\cdot}4 \times 10^3$

It will be seen that the dissociation constant of the complex intermediate compound between glucose and complex copper salt is 100 both when Fehling's solution and Benedict's solution are used. The value of K diminishes from 100 in the case of glucose complex, to 18 for the glycerine complex and to 10 for the sodium formate complex.

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Temperature Coefficients, Quantum Efficiency and the Relation between Intensity and Velocity of the Hydrolysis of Cane Sugar in Visible and Infra-red Radiations.

By A. K. Bhattacharya and N. R. Dhar.

A few years ago Lindemann (*Phil. Mag.*, 1920, *vi*, **40**, 671) pointed out that on the basis of the simple radiation hypothesis, the inversion of cane sugar must be enormously accelerated by sunlight but he stated that the reaction actually proceeds at the same rate whether it is exposed to sunlight or not. In publications from these laboratories (Dhar, *Z. anorg. Chem.*, 1921, **119**, 177; *Faraday Soc. Disc.*, 1921) it has been shown that the statement of Lindemann is not correct and that a solution of sucrose in tropical sunlight is completely inverted even in absence of acids on long exposure, whilst in presence of hydrochloric acid the inversion is distinctly accelerated by sunlight. In a subsequent communication, Banerji and Dhar (*Z. anorg. Chem.*, 1924, **134**, 172) investigated the kinetics of sucrose inversion in presence of hydrochloric acid in sunlight and showed that the temperature coefficient for a ten-degree rise of temperature can vary from 3·4 to 2·78 in sunlight according to the variations in light intensity, whilst the temperature coefficient of the dark reaction has a value 3·82 under the same conditions.

In this communication we are submitting the results obtained in the determination of temperature coefficients, quantum efficiency and the influence of variation of intensity on the hydrolysis of sucrose in light of different wave-lengths.

The experimental arrangement is the same as described in a previous paper (Bhattacharya and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 143).

The velocity of the hydrolysis of sucrose was determined by a polarimeter.

In order to determine the light absorption of cane sugar in different parts of the visible spectrum the extinction coefficients have been measured by a Nutting's spectrophotometer.

The following are the experimental results:—

Temperature = 30°. *Region* $\lambda = 4725$Å.

Time.	Reading on the polarimeter scale.	k_1 Monomolecular.
0 hours.	11·4	—
2	11·95	0·000146
4	10·50	0·000149
6	10·10	0·000146
	Mean	0·000147

20% *Cane sugar* (15 *c.c.*) *and* N/20-*Hydrochloric Acid* (5 *c.c.*).

Condition.	Temp.	k_1 Monomolecular.	k_1 After deducting the dark reaction.	Temp. coefficient.	Temperature coefficient after deducting the dark reaction.	Quantum efficiency.
Dark.	30°	0·0000975				
	35°	0·000189	—	3·85	—	—
	45°	0·000727				
(5000-4450Å)	30°	0·000147	0·0000495			—
Mean 4725Å	35°	0·000278	0·000089	—	3·18	455
	45°	0·00101	0·000283			630
(5850-5450Å)	30°	0·000125	0·0000275			250
Mean 5650Å.	35°	0·000242	0·000053	—	3·32	385
	45°	0·000903	0·000176			—
(7608-7000Å)	30°	0·0001096	0·0000121			145
Mean 7304Å.	35°	0·000212	0·000023	—	3·70	162
	45°	0·000812	0·000085			—
1000 Watt lamp	35°	0·000548	0·000359	—	—	$16·5 \times 10^9$
,, 10% Cane sugar	35°	0·000794	0·000522	—	—	20×10^9

Light absorption.

$$\text{Extinction coefficient} = \frac{\text{Density reading on the scale}}{\text{Thickness of the cell}}$$

Region in A. U.	7000	6500	5970	5600	5000	4800	4720	4550	4400
Extinction coefficient.	0·06	0·07	0·08	0·09	0·10	0·11	0·12	0·13	0·14

From the results recorded in the foregoing pages it will be observed that Einstein's law of photochemical equivalence is not at all applicable. The quantum efficiency increases with the temperature and concentration of the reacting system and the frequency of the incident radiation.

The experimental results show that in all cases the temperature coefficients of the photochemical changes are less than those of the corresponding thermal reactions. The greater the acceleration in light of different wave-lengths, the less the temperature coefficient.

It is believed that the photochemical reactions are brought about mostly by violet and ultra-violet radiations. Our experimental results however, prove that the inversion of sucrose and other chemical changes can be accelerated by radiation of wave-length 7304Å which lies in the infra-red region (*cf.* Bhattacharya and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 451). We have carefully measured the extinction coefficient of the reacting system by Nutting's spectrophotometer and have found appreciable absorption in the region 7000Å, It is apparent, therefore, that the reacting substances actually absorb the radiation wave-length of 7304 Å and are activated by the absorption of energy and then react chemically. We have also observed that the hydrolysis of sucrose can be accelerated by radiations of wave-lengths 5650Å and 4725Å and these wave-lengths are also appreciably absorbed by the reacting system.

According to the radiation hypothesis of Trautz (*Z. wiss. Phot.*, 1906, **4**, 106), Perrin (*Ann Physique*, 1919, **11**, 1) and Lewis (*J. Chem. Soc.*, 1914, **105**, 2330; 1915, **107**, 233) we can easily calculate from the temperature coefficient of the thermal reaction, the wave-length of the radiation which should accelerate the chemical change. The following result has been obtained :—

	Temperature coeff. (dark.)	Wave-length.
Hydrolysis of cane sugar.	3·85	1·19μ

We are of the opinion that the wave-lengths obtained by calculation from the thermal temperature coefficients may be regarded as the threshold limit. No acceleration of the sucrose inversion is possible with radiations of wave-lengths longer than 11900 Å. Our experimental results show that sucrose inversion is appreciably accelerated by

radiations of $\lambda = 7304$Å. The main difference between our conception and the Perrin-Lewis radiation hypothesis is that according to the latter view the wave-length calculated from the temperature coefficient should bring about the maximum speed of that reaction in question whilst according to the conception now put forward, the threshold frequency is the minimum frequency necessary for the carrying out of the reaction.

The Relation between Intensity and Velocity of the Hydrolysis of Cane Sugar.

The experimental arrangement is the same as described in a previous paper (Bhattacharya and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 197).

The following are the experimental results:—

20% *Cane sugar* (15 *c.c.*) *and* N/20-HCl (5 *c.c.*)

Temperature = 35°.

Diameter of aperture.	Area of the aperture.	k_1 Monomolecular.	k_1 After deducting the dark reaction velocity k_1 (dark) = 0·000189.
	A. *Source* 1000 *watt lamp.*		
2 cm.	3·14 sq. cm.	0·000548	0·000359 (I)
0·8	0·5024 ,,	0·000218	0·000059 (II)
	B. *Region* $\lambda = 5650$Å (from 1000 watt lamp).		
2	3·14 sq.	0·000228	0·000039 (I)
1	0·785 cm.	0·000195	0·00006 (II)

Ratio of velocities.	If directly proportional to the change in intensity.	If proportional to the square root of the change in intensity.
	A. *Source* 1000 *watt lamp.*	
$\frac{I}{II} = 6$	$\frac{3·14}{0·5024} = 6·25$	$\sqrt{6·25} = 2·5$
	B. *Region* $\lambda = 5650$Å (from 1000 watt lamp).	
$\frac{I}{II} = 6·5$	$\frac{3·14}{0·785} = 4$	$\sqrt{4} = 2$

In order to be sure that the light absorption varies proportionately with intensity of radiation, the following experiments were performed using a radiomicrometer.

Source.	Diameter of the aperture.	Absorption by the reacting system (deflection in cms.)
1000 watt-lamp.	2 cm.	0·3
	0·8	0·05

Ratio of intensity.	Ratio of absorption.
$\frac{I}{I1} = \frac{3·14}{0·5024} = 6·25$	$\frac{0·3}{0·05} = 6$

Variation of Quantum Yield with the Variation of Intensity.

Source 1000 *watt lamp.*

Diameter of the aperture.	Quantum efficiency.
2 cm.	$16·5 \times 10^3$
0·8	$19·2 \times 10^3$

From the foregoing results it will be evident that the relation between intensity and velocity of the hydrolysis of cane sugar varies from 1 to $\frac{3}{2}$ depending upon the ratio of the thermal and photochemical reactions.

In a foregoing paper we have obtained similar results with several other photochemical reactions. These results show that by increasing the velocity of the dark reaction and exposing it to radiation which is slightly absorbed by the reacting system a truly photochemical reaction which is proportional to the square root of the incident radiation, becomes directly proportional to the intensity of the incident radiation.

On the other hand, a photochemical reaction which is proportional to the square of the incident radiation or is directly proportional can be made to be proportional to the square root of the incident radiation by decreasing the dark reaction velocity and increasing the photochemical velocity.

From the measurements of the absorption of incident radiation by a radiomicrometer we find that the light absorption is directly proportional to the intensity of the incident radiation.

Hence we venture to suggest that the velocity of sucrose inversion is likely to be proportional to $I^{\frac{1}{2}}$ or $I^{\frac{1}{3}}$ when illuminated with intense ultra-violet radiations and that the relation between intensity or absorption of the incident radiation and the velocity of a photochemical reaction can vary from any proper fraction to 2 depending upon the ratio of the thermal and photochemical reaction velocities.

We have also determined the quantum yield with the variation of intensity and hence the absorption and have found that the quantum yield increases with the decrease of intensity, *i. e.*, the absorption.

Summary.

1. The temperature coefficients of the hydrolysis of cane sugar between 35° and 45° are 3·85 (dark), 3·18 ($\lambda=4725$ Å), 3·32 ($\lambda=5650$ Å) and 3·7 ($\lambda=7304$ Å).

2. The quantum yield is very high and it increases with the temperature and the frequency of the incident radiation.

3. The extinction coefficient measurements show that there is appreciable absorption in the region $\lambda=7000$ Å.

4. The absorption of light by an acid solution of sucrose varies proportionately with the intensity of the incident radiation. The same solution shows appreciable absorption of radiations of wavelengths from 4400 to 7000 Å.

5. The relation between intensity or the absorption of light and the velocity of the hydrolysis of sucrose varies from 1 to $\frac{3}{2}$ depending upon the velocities of the thermal and photochemical reactions.

6. The quantum yield increases with the decrease in intensity or the absorption of the incident radiation.

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Action of Bases on Complex Compounds derived from Organic Thio-compounds and Platinic Chloride.

By Prafulla Chundra Rây and Purna Chandra Mukherjee.

In continuation of the work on the action of organic thio-compounds upon chloroplatinic acid, the behaviour of methyl sulphide towards chloroplatinic acid has been studied and the following compounds have been isolated:—

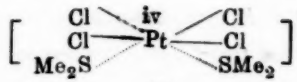
(*i*) $PtCl_4 \cdot 2(CH_3)_2S$; (*ii*) $PtCl_3 \cdot 2(CH_3)_2S$; (*iii*) $PtCl_2 \cdot 2(CH_3)_2S$.

These compounds have been subjected to the action of bases like ethylamine, pyridine, etc., and a study of the resulting products has been found to throw considerable light on the constitution of the parent bodies (*cf.* Rây, Guha and Bose-Rây, *J. Indian Chem. Soc.*, 1926, **3**, 155; Rây, Bose-Rây and Adhikary, *ibid*, 1927, **3**, 476; Rây, Bose-Rây and Rây-Chowdhury, *ibid*, 1928, **5**, 139).

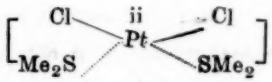
The products are mostly well-known compounds of the Werner type, some of which have already been obtained by previous workers by the action of bases on similar complex compounds of platinum (Rây and collaborators, *loc. cit.*). This suggests that the compounds (*i*), (*ii*) and (*iii*) possess the Werner constitution.

Constitution of $PtCl_4 \cdot 2Me_2S$, *etc.*

The compounds $PtCl_4 \cdot 2Me_2S$ and $PtCl_2 \cdot 2Me_2S$ may be represented as normal compounds of quadri- and bi-valent platinum respectively.



(*i*)



(*ii*)

That the compound (*i*) is practically a non-electrolyte has been shown by conductivity measurement in acetone solution, thus supporting the constitution given.

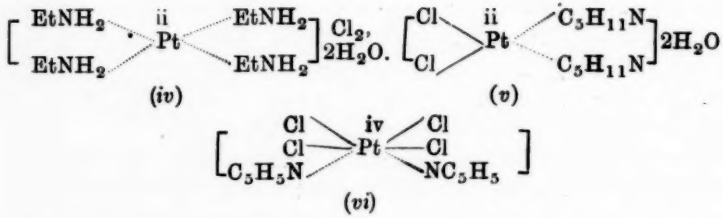
The compound (*ii*) $PtCl_3 \cdot 2Me_2S$, when boiled vigorously with water, breaks up into $PtCl_4 \cdot 2Me_2S$ and $PtCl_2 \cdot 2Me_2S$.

Action of Bases on $PtCl_4 \cdot 2Me_2S$.

By the action of ethylamine, piperidine and pyridine respectively upon $PtCl_4 \cdot 2Me_2S$, the following compounds have been obtained: –

(*iv*) $PtCl_2 \cdot 4EtNH_2 \cdot 2H_2O$; (*v*) $PtCl_2 \cdot 2C_5H_{11}N \cdot 2H_2O$. (*vi*) $PtCl_4 \cdot 2C_5H_5N$

In the componds (*iv*) and (*v*) the platinum is bivalent while in (*vi*) it is tetravalent. So it is evident that in some cases the compound $PtCl_4 \cdot 2Me_2S$ is reduced and at the same time the Me_2S radicles are replaced by the bases, but in the other, the valency of platinum is not altered, the base simply replacing the sulphide radicles. The constitution of the compounds may be represented as follows: —



(*iv*) (*v*) (*vi*)

The complete ionisability of the chlorine atoms in (*iv*) was proved directly. No ionising solvent for the compound (*v*) however could be found, so that its constitution could not be proved directly. The compound (*vi*) is well-known and can have no other coustitution than that suggested above.

Experimental.

Action of Methyl Sulphide upon Platinic Chloride.

An excess of methyl sulphide was added to an aqueous solution of platinic chloride at the ordinary temperature. The whole was then cooled in ice-water as the heat evolution during the reaction was very great. As the reaction proceeded, orange yellow mealy crystals began to settle down. After an hour, when the reaction was complete, the crystalline product was filtered from the mother-liquor

and washed successively with water, alcohol and acetone. The purified compound was then dried in a vacuum. (Found: Pt, 45·74 ; Cl, 24·55 ; S, 14·82. $PtCl_3 \cdot 2Me_2S$ requires Pt, 45·82 ; Cl, 25·03 ; S, 15·07 per cent.).

The mother-liquor, on evaporation, gave an impure product which was perhaps a mixture of different compounds.

Preparation of the Compounds $PtCl_4 \cdot 2Me_2S$ *and* $PtCl_2 \cdot 2Me_2S$.

The compound $PtCl_3 \cdot 2Me_2S$ was boiled with water for a long time and filtered hot in the pump. A part of the compound went into solution. The process was repeated several times until the soluble constituent had been completely removed. The insoluble residue was dried. It dissolved in boiling acetone from which it separated out as bright yellow crystals. (Found: Pt, 42·20 ; Cl, 30·51 ; C, 9·78 ; H, 2·67 ; S, present. $PtCl_4 \cdot 2Me_2S$ requires Pt, 42·29 ; Cl, 30·80 ; C, 10·41 ; H, 2·61 ; S, 13·9 per cent.).

The aqueous extract was evaporated in a vacuum desiccator over sulphuric acid and a pale yellow crystalline compound was obtained. This was twice recrystallised from water. (Found: Pt, 49·80 ; Cl, 17·66, S, present. $PtCl_2 \cdot 2Me_2S$ requires Pt, 50·00 ; Cl, 18·20 ; S, 16·4 per cent.).

This compound has also been obtained by a different method (Blomstrand, *J. pr. Chem.*, 1888, *ii*, **38**, 359; Klusom, *ibid*, 1903, *ii*, **67**, 24).

Conductivity Measurement of $PtCl_4 \cdot 2Me_2S$ *in acetone solution.*

Weight of the substance taken = 0·6657 gm. Cell constant = 0·1535.

Dilution.	Observed resistance.	Calculated molecular conductivity.
69260 c.c.	13600 ohms.	0·6688
138520	23200	2·17

The very low molecular conductivity shows that the compound is not ionised in the solvent, thus agreeing with the constitution of the substance suggested previously.

Action of Bases on $PtCl_4 \cdot 2Me_2S$.

(*a*) *Ethylamine*. On mixing $PtCl_4 \cdot 2Me_2S$ and an excess of aqueous ethylamine (30%) great heat was evolved and the platinum compound gradually went into solution. On concentration of the solution white crystals began to separate out. These were filtered off, washed with a little water and recrystallised from it. The compound

melts with decomposition at 211°. (Found: Pt, 40·20 ; Cl, 14·85 ; N, 11·85. $PtCl_2 \cdot 4EtNH_2 \cdot 2H_2O$ requires Pt, 40·48 ; Cl, 14·73 ; N, 11·62 per cent.). Sulphur was found to be absent.

(*b*) *Piperidine*. $PtCl_4 \cdot 2Me_2S$ and an excess of piperidine were thoroughly mixed, when much heat was evolved. The mixture was then heated on a water-bath for fifteen minutes to complete the reaction. The bright yellow colour of the compound changed to yellowish white. The insoluble mass was then filtered, washed with a little piperidine and then digested with water to remove piperidine hydrochloride formed during the reaction. The residue was then washed with water, alcohol and ether and dried in a vacuum. (Found: Pt, 41·28 ; Cl, 15·64 ; N, 5·80 ; S, absent. $PtCl_2 \cdot 2C_5H_{11}N \cdot 2H_2O$ requires Pt, 41·31 ; Cl, 15·04 ; N, 5·93 per cent.).

(*c*) *Pyridine*. $PtCl_4 \cdot 2Me_2S$ and an excess of pyridine were thoroughly mixed. The mixture was then heated on a water-bath for 15 minutes and then filtered, washed with a little pyridine and then with water to remove pyridine hydrochloride formed during the reaction. The residue was then washed with alcohol and ether and dried in a vacuum desiccator. The compound forms yellow crystals. (Found: Pt, 39·08; Cl, 28·27; N, 5·48; S, absent. $PtCl_4 \cdot 2C_5H_5N$ requires Pt, 39·39; Cl, 28·6; N, 5·65 per cent.).

This compound had previously been obtained by Rây, Guha and Bose-Rây (*J. Indian Chem. Soc.*, 1926, **3**, 160) by a different method.

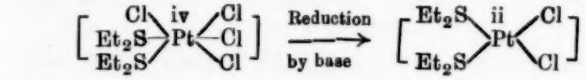
Action of Bases on $PtCl_4 \cdot 2Et_2S$.

The action of the four bases, *e.g.*, aniline, benzylamine, ammonia and pyridine on $PtCl_4 \cdot 2Et_2S$ has already been described (Rây, Guha and Bose-Rây, *J. Indian Chem. Soc.*, *loc. cit.*, pp. 157, 361). In the former paper the authors showed that the bases ammonia and pyridine on interaction with $PtCl_4 \cdot 2Et_2S$ simply replace the two sulphide radicles and in the latter paper the authors have shown that the tetravalent platinum is first reduced to the bivalent condition by the action of aniline and benzylamine and then the two sulphide radicles are replaced by two or four molecules of the base.

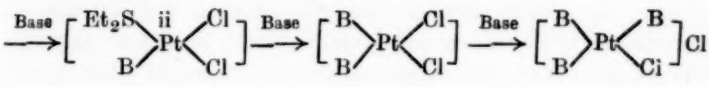
In the present work it has been shown that, after the reduction of platinum from the tetravalent to the bivalent stage, the replacement of the two sulphide radicles takes place step by step, and intermediate compounds are sometimes obtainable. In some cases when the base is very reactive, the replacement of the two sulphide

radicles takes place so rapidly that no intermediate compound could be isolated. But in the case of some other bases, *e.g.*, diethylamine, trimethylamine, etc., the reaction may be arrested at the intermediate stage.

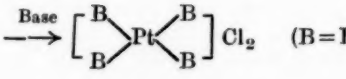
The following scheme illustrating the principle suggested:—



(*vii*)



(*viii*) (*ix*) (*x*)



(B = Base).

(*xi*)

The formation of compounds of the type (*vii*), (*ix*), (*x*) and (*xi*) has already been noticed (*loc. cit.*). A compound of the type (*viii*) and that intermediate between (*vii*) and (*viii*) have been isolated during the present investigation, *e.g.*,

(*xii*) $PtCl_2 \cdot Et_2S \cdot Et_2NH$ (Type *viii*)

(*xiii*) $Pt_2Cl_4 \cdot 2Et_2S \cdot Et_2NH$ (Type intermediate between *vii* and *viii*)

(*xiv*) $PtCl_2 \cdot Et_2S \cdot Me_3N$. (Type *viii*)

Action of Bases on $PtCl_4 \cdot 2Et_2S$.

(*a*) *Diethylamine.* $PtCl_4 \cdot 2Et_2S$ was treated with an excess of diethylamine (30% aqueous soln.) and the whole was allowed to stand overnight. This was then filtered and washed with water to remove completely the hydrochloride of the base formed during the reaction. It was then further washed with alcohol and ether and dried in a vacuum over sulphuric acid. The compound was pale yellow and insoluble. (Found: Pt, 45·05; Cl, 16·95; S, 7·19; N, 3·16. $PtCl_2 \cdot Et_2S \cdot Et_2NH$ requires Pt, 45·45; Cl, 16·55; S, 7·46; N, 3·26 per cent.).

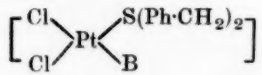
The aqueous mother-liquor from the above preparation yielded, on concentration in a vacuum, a yellow crystalline compound. It was filtered, washed with a little water and then with alcohol and ether. It was then dried in a vacuum over sulphuric acid. (Found: Pt, 49·33; Cl, 18·24; N, 1·81. $Pt_2Cl_4 \cdot 2Et_2S \cdot Et_2NH$ requires Pt, 49·98; Cl, 18·10; N, 1·78 per cent.). Sulphur was found to be present qualitatively.

(*b*) *Trimethylamine*. Solid $PtCl_4 \cdot 2Et_2S$ was treated with an excess of alcoholic solution of trimethylamine and the mixture was kept for three days in a flask which was tightly corked. The platinum compound gradually went into solution. The solution was filtered and to the filtrate ether was added. A yellow precipitate came down. This was collected and crystallised from ether in which it was not easily soluble. (Found: Pt, 46·69; Cl, 16·66; S, 7·11; N, 3·43. $PtCl_2 \cdot Et_2S \cdot NMe_3$ requires Pt, 45·98; Cl, 17·10; S, 7·71; N, 3·38 per cent.).

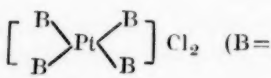
Action of Bases on $PtCl_3 \cdot 2(Ph \cdot CH_2)_2S$.

The above compound and the action of some bases on it have already been discussed (Rây, Bose-Rây, and Rây-Choudhury, *J. Indian Chem. Soc.*, 1928, **5**, 139). In the present work action of several other bases on the compound has been studied and the products obtained have been found to agree in some cases with the mode of reaction given in the said communication.

Further compounds of the types (*xiv*) and (*xv*) have been isolated in the present investigation.



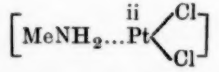
(*xiv*) (B = Et_2NH).



(*xv*)

By the action of methylamine on $PtCl_2 \cdot (Ph \cdot CH_2)_2S$, the compound $PtCl_2 \cdot MeNH_2$ has been obtained. Here two molecules of benzyl sulphide are replaced by one molecule of the base with

simultaneous reduction. The compound may be represented by (*xvi*)



(*xvi*)

Action of Bases upon $PtCl_3 \cdot 2(Ph \cdot CH_2)_2S$.

(*a*) ***Propylamine.*** $PtCl_3 \cdot 2(Ph \cdot CH_2)_2S$ was treated with an excess of anhydrous propylamine at 0° and the mixture was kept overnight in a closed vessel. The mass became viscous. On the addition of water the brown colour of the mass disappeared and a white precipitate separated out. This was filtered and washed with water and alcohol. The product was crystallised from hot water when colourless needles, m.p. 198° with decomposition, were obtained. (Found: Pt, 36·57; Cl, 13·47; C, 26·39; H, 7·44. $PtCl_2 \cdot 4C_3H_7NH_2 \cdot 2H_2O$ requires Pt, 36·24; Cl, 13·19; C, 26·76; H, 7·74 per cent.) Sulphur was found to be absent.

(*b*) ***Diethylamine.*** A mixture of $PtCl_3 \cdot 2(Ph \cdot CH_2)_2S$ and an excess of diethylamine was kept for two days in an air-tight flask. An insoluble yellow compound gradually settled down. This was filtered, washed with water and then with alcohol. The yellow mass was then crystallised from benzene, filtered, washed with alcohol and ether. (Found: Pt, 35·93; Cl, 13·85; S, 5·13; N, 2·61. $Ph \cdot CH_2S \cdot PtCl_2 \cdot Et_2NH$ requires Pt, 35·20; Cl, 12·82; S, 5·79; N, 2·53 per cent.).

(*c*) ***Diethylamine.*** An excess of methylamine (alcoholic solution) was treated wfth $PtCl_3 \cdot (Ph \cdot CH_2)_2S$ at 6° and kept overnight in a closed vessel when the substance went into solution from which a light greenish crystalline compound separated out. This was filtered and washed repeatedly with boiling benzene to remove any unchanged $PtCl_3 \cdot 2(Ph \cdot CH_2)_2S$. The residue was then washed with alcohol and then with water to remove the hydrochloride of the base formed during the reaction. The purified compound was finally washed with alcohol and ether and dried in a vacuum desiccator. (Found: Pt, 65·75; Cl, 23·14; N, 4·78. $PtCl_2 \cdot MeNH_2$ requires Pt, 65·65; Cl, 23·90; N, 4·71 per cent.).

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Studies in Silicic Acid Gels. Part II. The Hydrogen-ion Concentration and Cataphoresis of the Gel-forming Mixtures.

By Mata Prasad and R. R. Hattiangadi.

It has been shown by Prasad and Hattiangadi (*J. Indian Chem. Soc.*, 1929, **6**, 653) that on mixing solutions of neutral ammonium acetate of various concentrations to the same solution of sodium silicate, the time of setting of the gels decreases as the concentration of ammonium acetate is increased; high concentrations give flocculent precipitates instead of gels. But with acidic ammonium acetate, as its concentration increases, the time of setting at first decreases, reaches a minimum and then begins to increase. It has also been shown that the time of setting of the gels is considerably delayed in moderately acidic and highly alkaline medium and that the gels formed in their respective presence differ from each other in transparency.

Such a be haviour of acidic ammonium acetate is similar to that of acids as ha s been observed by Fleming, Holmes, and Fells and Firth. According to Fleming (*Z. Physik*, 1902, **41**, 427) the time of setting of the gel is governed by the catalytic effect of the H- and OH-ions ; but Holmes (*J. Phys. Chem.*, 1918, **22**, 510) concluded from his investigations that the dehydrating influence of the non-ionised molecules of the acids mixed with sodium silicate solutions was an important factor in controlling the setting of the gels. Fells and Firth (*J. Phys. Chem.*, 1925, **29**, 241) are also of the opinion that the time of setting of the silicic acid gel is not mainly governed by the H-ion concentration of the mixture but is influenced by the catalytic effect of the non-ionised molecules of the acids.

An attempt has, therefore, been made to study the hydrogen ion concentrations of the gel-forming mixtures and as the peculiar behaviour of the acidic ammonium acetate is due to the presence of free acetic acid in it, acetic acid instead of acidic ammonium acetate has been used in all the mixtures. The nature of silicic acid

in the acidic and alkaline mixtures has also been determined and the results obtained have thrown considerable light on the mechanism of gelation.

The hydrogen-ion concentration and the time of setting of mixtures of sodium silicate and other acids have also been studied in order to obtain definite knowledge of the role played by the H- and OH-ions and to determine the nature of the influence of different ions on the gel-forming mixtures.

Determination of the p_H values of the gel-forming mixture.

Kruyt and Postma (*Rec. trav. chim.*, 1925, **44**, 765) have studied the changes in the p_H values of the silicic acid sol during dialysis and have used the electrometric method for these measurements. In the present investigation the indicator method of measuring the p_H was employed. This method is more useful though not as accurate as the electrometric one, as the measurements can be made in a very short time. This is very necessary as the p_H of some of the mixtures changes very rapidly with time. Also some gels set in a few seconds and the latter method which involves the bubbling of hydrogen, cannot be used here as this process will disturb the gel formation (*cf.* Part I).

The sodium silicate used in this investigation was Na_2O, $2{\cdot}33SiO_2$. A solution of 4 per cent. silica content titrated with 0·57 *N*-acid. Pyrex glass test-tubes which were thoroughly cleaned and dried were used for keeping the standard tints as well as the reaction mixtures. The buffer solution was prepared from B. D. H. "Universal buffer solution" which has an initial p_H of 3·1 and varies with the addition of 0·2*N*-NaOH or 0·2*N*-HCl according to the formula,

$$\text{Final } p_H = 3{\cdot}1 \pm 1{\cdot}185V$$

where V is the volume of the acid or alkali added.

Sodium hydroxide solution was prepared from Merck's extra pure sticks by making a saturated solution of caustic soda in redistilled water in Pyrex glass flasks and keeping it for 48 hours to allow the carbonate formed to settle to the bottom. The clear supernatant liquid was pipetted out and was carefully standardised. Hydrochloric acid solutions were prepared from Merck's pure compound.

The indicators used were B. D. H. chemicals and their concentrations employed were as obtained from British Drug House, Ltd. Only those of them were utilised, which had been used by Clarke, Lubs and Sörensen and had been shown to be free from many abnormalities.

The approximate p_H values of the gel-forming mixtures were first determined by the use of the 'Universal Indicator' supplied by the British Drug House which has a p_H range of 3 to 10. For accurate determinations 5 c.c. of the sodium silicate solutions were mixed with 5 c. c. of an acid in a pyrex glass tube to which 0·1 c. c. of the required indicator is already added. The tint of this mixture was laterally compared with the standard tints against clean white porcelain tiles. The stop-watch was started simultaneously with the mixing and the time of setting of the gel was also recorded. The change in p_H with the progress of time, if any, was also measured in the same way. But in these cases the slow coagulation of silicic acid produced an increasing turbidity in the reaction mixture and it was difficult to obtain the exact colour match with the standards. Neither was it possible to precipitate barium sulphate in the standard tints as suggested by Clark ("Determination of Hydrogen Ions", p. 71) to overcome this difficulty add to make them correspond with the reaction mixtures as the turbidity of the latter varied with time. In these experiments, therefore, great accuracy is not claimed but the discretion used to differentiate the various p_H values could give reproducible results. Besides, the indicators used being alcoholic solutions of organic substances, another factor has been introduced, caused by the specific influence of the alcohol on the gel-forming mixtures.

The results obtained with acetic acid in the alkaline and acid mixtures are given in the following tables:—

TABLE I.

Concentration of SiO_2=2%. Reaction acidic.

Strength of acetic acid.	p_H.	Time of setting.
0·35*N*	5·4	10½ hrs.
0·325*N*	5·5	5 ,, 27 mins.
0·30*N*	6·2	1 hr. 2 ,,

There is no appreciable change in the p_H values during or after gelation.

TABLE I *a*.

Concentration of SiO_2 = 2%. Reaction alkaline.

Strength of acetic acid.	p_H.	Time of setting.
0·285*N*	Initial p_H 7·2, changes rapidly to 7·4 in 10 mins. and then to 7·7.	39 mins.
0·275*N*	Initial p_H 7·9, in 15 mins. 8·2, after complete gelation colour deepens corresponding to 8·4 p_H.	75 mins.
0·25*N*	Initial *p*H 8·6, changes rapidly to 9·35	Abont a week.

TABLE II.

Concentration of SiO_2 = 3%. Reaction acidic.

Strength of acetic acid.	p_H.	Time of setting.
0·525*N*	5·3	4 hrs. 5 mins.
0·487*N*	5·5	2 48
0·45*N*	6·1	0 55

There is no appreciable change in the p_H during or after gelation.

TABLE II*a*

Concentration of SiO_2 = 3%. Reaction alkaline.

Strength of acetic acid.	p_H	Time of setting.
0·412*N*	Initial p_H = 7·2, changes rapidly to 7·7.	7 mins.
0·4*N*	Initial p_H = 7·55, changes rapidly to 8·2.	10 ,,
0·375*N*	Initial p_H = 8·5, rapidly changes to 8·6.	53 ,,

TABLE III.

Concentration of SiO_2 = 4%. Reaction acidic.

Strength of acetic acitic.	p_H.	Time of setting.
0·7*N*	5·3	2 hrs.
0·65*N*	5·58	58 mins.
0·6*N*	6·2	13 ,,

TABLE III*a*.

Concentration of SiO_2 = 4%. Reaction alkaline.

Strength of acetic acid.	p_H.	Time of setting.
0·575*N*	7·1 – 7·2, after 24 hrs. 7·6	5½ mins.
0·55*N*	7·69, changes to 8·2, 8·8	3½
0·525*N*	8·2, rapidly changes to 8·8	4½
0·50*N*	8·6, rapidly changes to 9·3	9½

TABLES IV and IV*a*.*

Concentration of $SiO_2 = 5\%$.

	Initial p_H.	Time of setting.
Acidic.	5·4	63 mins.
	5·65	30 ,,
	6·2	8 ,,
	7·8	1½ ,,
	8·4	2 ,,
	9·8	5 ,,
Alkaline.	10	7½ ,,
	10·2	38 ,,
	10·4	3 hrs.
	10·6	10 ,,

It will be seen from the foregoing tables that the p_H of the mixtures changes with the change in concentrations of silica and

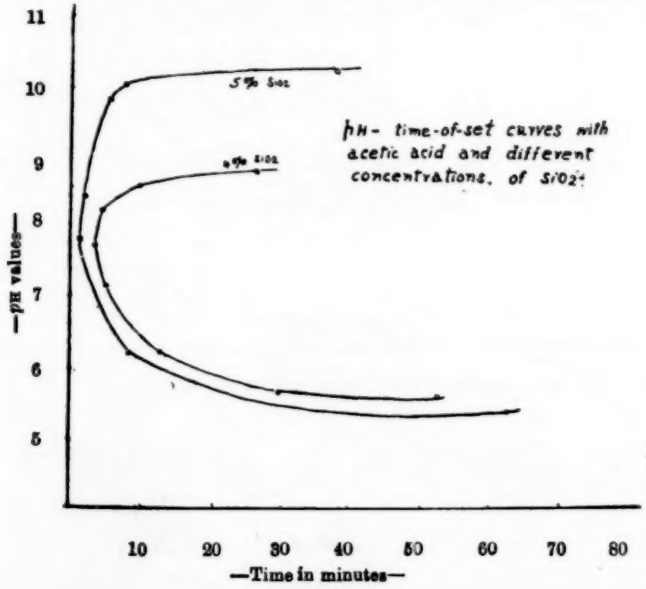

Fig. 1.

the acid. It will be further noted from Fig. 1 that the minimum time of setting does not occur at one particular p_H of the gel-form-

* In this table mixtures having a p_H of less than 7 *i.e.*, which are acidic do not show any appreciable change in the p_H values during or after gelation. But those above $p_H = 7$ show considerable changes in the p_H values as observed in preceding cases.

ing mixtures but depends upon the concentration of silica and is higher, the greater is the silica content of the mixture.

The effect of hydrochloric and sulphuric acids on the p_H values and the time of setting mixtures was next studied and the results obtained have been compared with those of acetic acid in the following tables.

TABLE V.

Concentration of SiO_2=4%.

p_H.	Time of set with acetic acid.	p_H.	Time of set with HCl.	p_H.	Time of set with H_2SO_4
5·3	2 hrs.	5·15	2 hrs.	5·6	35 mins.
5·58	53 mins.	5·6	24 mins.	5·7	21½ ,,
6·2	13 ,,	5·7	13½ ,,	5·75	14½ ,,
7·1	5½ ,,	6·2	5½ ,,	5·8	12 ,,
7·7	3½ ,,	7·8	1⅝ ,,	6·8	4 ,,
8·2	4½ ,,	8·4	6½ ,,	7·2	3½ ,,
8·6	9½ ,,	8·8	12½ ,,	7·9	2½ ,,
...	...	9·0	27 ,,	8·6	13 ,,
...	...	...	...	8·8	50 ,,

TABLE VI.

Concentration of SiO_2=5 %.

p_H.	Time of setting with acetic acid.	p_H.	Time of setting with HCl.
5·4	63 mins.	5·4	18½ mins.
5·65	30 ,,	5·52	14
6·2	8 ,,	5·6	10
7·8	1½ ,,	5·9	3 45 secs
8·4	2 ,,	6·2	2 45 ,,
9·8	5 ,,	7·4	1 5 ,,
10·2	38 ,,	7·95	0 50 ,,
10·4	3 hrs.	9·35	7 mins.

It appears from the above that for the same p_H, acetic, hydrochloric and sulphuric acids give different times of setting. This probably depends on the influence of the other ions in the mixture, namely, acetate, chloride and sulphate. It will be further seen that when the p_H is below 7, that is, the mixtures are acidic, hydrochloric acid gives a gel earlier than sulphuric acid which again gives it earlier than acetic. But when the p_H is above 7, that is, the mixtures are alkaline, sulphuric acid delays the time of setting more than acetic or hydrochloric acids as shown in the p_H-time of setting curves (Fig. 2).

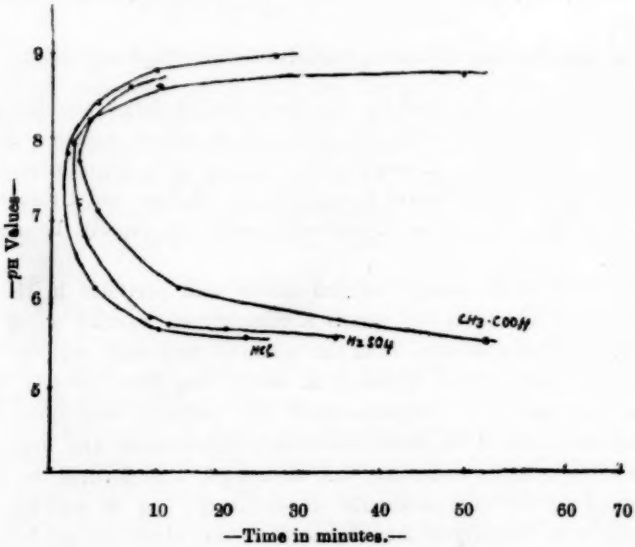

FIG. 2.

p_H—time-of-set curves with 4% SiO_2 and HCl, H_2SO_4 and CH_3·COOH.

Cataphoresis of the gel forming mixtures.

It has been shown by Billiter (*Z. physikal. Chem.*, 1905, **51**, 150) by cataphoretic experiments that the silicic acid sol is negatively charged in alkaline and feebly acidic solutions, and positively, at higher hydrogen ion concentrations. Lösenbeck (*Koll. Chem. Beihefte.*, 1922, **16**, 27) has measured the migration velocity of the silicic acid sol particles with different concentrations of hydrochloric acid and found that the particles were negatively charged at first, but the

charge decreased continuously with increasing amounts of the acid, reached the iso-electric point and then reversed until the positive charge carried by the particles was much greater than the original negative charge. Similar observations have been made by Perrin (*Compt. rend.*, 1903, **136**, 1388) and Pauli (*Beitr. chem. Physiol. Path.*, 1906, **7**, 531,) in the case of albumin sols.

Sodium silicate undergoes hydrolysis as

$$Na_2SiO_3 + 2H_2O = 2NaOH + H_2SiO_3.$$

The addition of neutral or acidic ammonium acetate may either hasten the hydrolysis or actually take part as a component of the reaction,

$$2CH_3COONH_4 + Na_2SiO_3 = 2CH_3COONa + H_2SiO_3 + 2NH_3.$$

The latter view is supported by the fact that a large amount of ammonia is evolved when the two solutions are mixed together and the gel on drying gives out needle-like crystals of sodium acetate. The silicic acid freshly formed is, according to Mylius and Groschuff (*Ber.*, 1906, **39**, 116), in the crystalloidal state but rapidly becomes colloidal.

The nature of the charge on the silicic acid particles in these mixtures was determined by means of cataphoresis carried on in a U-tube. Mixtures selected from the alkaline and acid regions for this purpose, were those which took fairly long time to set. On passing a current, a slow movement of the particles was observed towards the anode in the alkaline mixtures and towards the cathode in the acidic ones for sometime, and then a gel was formed in the anode and cathode compartments respectively. As is well-known the migration velocity of the emulsoids is very slow, and gel formation occurs in the limbs of the U-tube due to the neutralisation of the charge.

The p_H values of these mixtures were also measured by the method already described and the results obtained are the following:—

TABLE VII.

Mixture.		p_H.	Charge.
0·45*N* acetic acid and 4% SiO_2	...	10·1	Negative.
0·5*N* ,, ,,	...	8·6	,,
0·64*N* ,, ,,	...	5·7	Positive
0·7*N* ,, ,,	...	5·3	,,
25 % Am. acetate etc. ,,	...	5·5	,,

It will be seen from the above table that the reversal of the charge takes place at a very early stage, *i.e.*, when the mixtures are even slightly acidic. Kruyt and Postma (*loc. cit.*) have shown that the silicic acid sol is discharged at a $p_H = 2{\cdot}5$, and until then the addition of hydrochloric acid to the sol produced no change in the nature of the charge. The difference in the reversal of the charges in the two cases referred to above may be ascribed to the fact that the above mixtures are undialysed sols of silicic acid and thus differ from the pure sols which are negatively charged even at a $p_H = 4{\cdot}5$.

Discussion of Results.

The experiments on the cataphoresis of the various mixtures and the movement of the particles towards the electrodes indicate definitely the existence of colloidal particles in these mixtures. These particles have further been shown to be positively and negatively charged in the acidic and alkaline media respectively.

It will be seen from the results given in these pages that the minimum time of setting of the gels does not occur at the p_H value = 7 (Fig. 1) but is always higher. The minimum point in Fig. 2 (Part I) does not therefore indicate that mixtures containing higher concentrations of ammonium acetate than represented by this point are acidic or that the colloidal particles in these mixtures are positively charged.

Recent work of Powis (*Z. physikal. Chem.*, 1914, **71**, 179, 186; *J. Chem. Soc.*, 1916, **109**, 734) on an emulsion of a hydrocarbon oil in water, and colloidal arsenious sulphide, indicates that there is a critical value of the contact potential, not necessarily zero (neutral point) at or below which coagulation takes place easily.

As the gel formation from the mixtures studied here probably takes place by the coagulation of the silicic acid sol formed in these mixtures, the time of setting may be expected to be minimum at the isoelectric point of the sol particles. Assuming that the zero P. D. on the particles is indicated by the neutrality ($p_H = 7$) of the gel-forming mixtures, it appears that the P. D. on the silicic acid sol, in mixtures setting in minimum time, is not reduced to zero, but the particles still possess some small negative contact potential. An idea of the critical value of the negative contact potential on the particles can be obtained by the magnitude of the

difference in the p_H values of the mixtures at the minimum and neutral points (p_H=7) and is shown in the following table:—

TABLE VIII.

Neutral point p_H=7.

Concentration of SiO_2	p_H at minimum time.	Difference.
2 %	7·2	0·2
4 %	7·69	0·69
5 %	7·8	0·8

It will be seen from the above table that the critical potential for a colloidal solution of the same substance depends upon its concentration.

Mukherjee, Chaudhury and Choudhuri (*J. Indian Chem. Soc.*, 1927, **4**, 493) during their investigation of the rate of migration of sols have found that the rate of migration of sols of As_2S_3, gold, and $CuFe(CN)_6$ diminishes with dilution, *i.e.*, the density of charge decreases and the sols are rendered more unstable.

It will further be seen from Tables I*a* to IV*a* that when the mixtures are alkaline, the p_H values increase during and after gelation. This suggests therefore that some change, probably the hydrolysis of some unchanged sodium silicate, is taking place even after the gel has set.

When the mixtures are acidic, there are no perceptible changes in the p_H values during or after gelation. It appears, therefore, that during gelation from acidic mixtures, probably, only the neutralisation of the positive charge by the anions present in the mixture is taking place. The behaviour of sulphuric acid in the latter mixtures is, however, not in conformity with the Schulze-Hardy law of the coagulation of colloids. Sulphuric acid having a divalent anion is expected to be a better coagulant of the positive sol than hydrochloric or acetic acid. But the reverse has been observed to be the case.

It appears from the above discussion that the time of setting of a gel depends mainly, besides other factors such as viscosity and interfacial tension, upon two factors: (*i*) the density of the charge on the colloid particles which again is controlled by the relative adsorption of negative and positive ions—may be H- and OH-ions by the particle ; (*ii*) the effective concentration of the coagulating agent present in the mixtures.

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On the Variation of the Surface Tension of Aqueous Solutions of certain Dyestuffs with Time.

By J. C. Ghosh and Suresh Chandra Dutt.

The growth of films on the surface of aqueous solutions of a number of organic dyes was first recorded by Rhode (*Ann. Phys.*, 1906, **19**, 935). His method consisted in the suspension of a sheet of metal in the dye solution by a fine wire. Torsion was applied until the surface was broken. The angle of torsion was a measure of the thickness of the film, and the rate at which the torsion necessary for tearing of the film increases with time is a measure of the rate of growth of film. He concluded that the dyestuffs which in solution, show photo-electric effect, have the characteristic property of forming a film on the surface, the maximum photo-electric effect being obtained when the film thickness becomes maximum.

It appears that if a method could be devised for recording the variation of surface tension of these aqueous solutions of dyestuffs with time, some insight can be gained into the kinetics of the molecular processes which are responsible for producing a film on the surface. It is to be expected that with the growth of film on the surface, the surface tension of the solution should gradually diminish arriving at a constant value when the growth of the film is at an end.

Indications are not wanting that the nature of the surface of a solution immediately after it is created is different from that of the surface after a certain time has elapsed and conditions of equilibrium have been established. This is specially true in the case of hydrophyllic sols like sodium oleate, gelatine, egg-albumin, saponin, etc. For these sols, the investigations of Rayleigh (*Proc. Roy. Soc.*, 1890, **47**, 281) and Berczeller (*Intern. Z. physik-chem. Biol.*, 1914, **1**, 124) have shown that the surface tension mesured by a dynamic method—where the surface tension of a freshly created surface is measured—is always considerably greater than that measured by a static method. The reason for this difference is not far to seek. In a freshly created surface of these sols, the surface concentration of the micellæ is initially very small, much below the equilibrium surface concentration; and since the velocity of translation of these micellæ is much smaller than that of truly dissolved substances, the time required to reach static equilibrium at the surface is fairly long. Though the dynamic and static methods of measuring surface tension reveal that in case some hydrophyllic sols static equilibrium at

the surface is reached fairly slowly, no method has yet been devised for recording in these cases the rate of change of surface tension as the fresh surface gradually ages and reaches equilibrium conditions.

It is well known that aqueous solutions of many dyestuffs of very large molecular weight cannot be considered as true molecularly dispersed solutions. There is strong evidence of micellæ formation in many cases, and it is therefore to be expected that in these cases also, the freshly created surface should have a much larger surface tension than a surface which has been formed for a considerable time.

According to Freundlich "the method of adhesion of rings is to be particularly recommended for determining the surface tension of any plane liquid surface which it is desired to disturb as little as possible." In the experiments to be described in the following pages, the ring method has been suitably modified to yield values of surface tension of a surface at different intervals of time, not only without actually breaking the surface but also without disturbing the surface to any considerable extent.

Experimental.

To obtain accurate and satisfactory results, it is necessary to have a balance in which the weights required to counterbalance the forces of surface tension could be continuously but very slowly increased. From one end of the balance beam (Fig. 1) was therefore

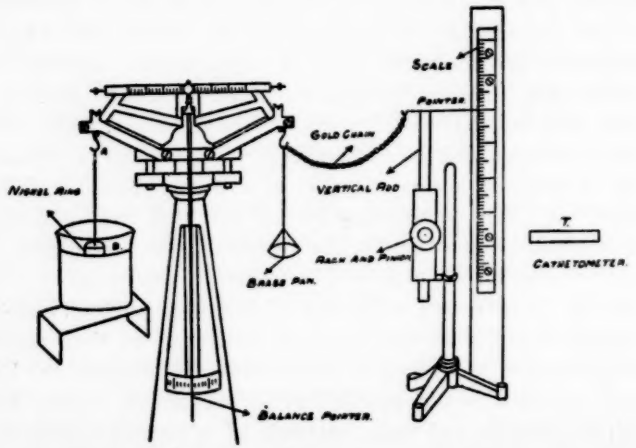

Fig. 1.

hung a fine gold chain; the other end of this chain was fastened to a vertical rod which could be moved up and down by means of a rack and pinion arrangement. A pointer attached to this vertical rod reads off its position against a vertical scale. The weight required to counterbalance the chain in different positions, was determined. The balance pan at *A* was replaced by an exactly circular basin *B* made of thin nickel plate. Suspension was effected by means of a copper rod soldered to the centre of the plate. The basin was so made that the lower rim, which was to touch the liquid surface, lay exactly in a horizontal plane when suspended from the hook *A*. In order that readings might be taken always at the same level of the surface of the solution, a cathetometer *T* was used for observing the height of the surface. It was found that in course of several hours the level of the surface fell due to evaporation. To avoid this difficulty water at about 40° in a large vessel was placed inside the balance case. The evaporation from this surface kept the humidity in the balance almost at saturation. The level of the solution remained constant without the temperature fluctuating more than 0·5° during the course of the experiment.

A glass beaker containing water was placed beneath the inverted nickel basin, the balance beam freed from arrestment, and when oscillations had ceased, water was poured in until the lower rim completely touched the surface of the water. Weights were then added to the other end of the balance beam, the final additions being made by lowering the chain. The pointer attached to the balance remained motionless until a critical weight has been added when it began to move to the left, indicating that the weight has counterbalanced the forces of surface tension. This motion is slow and the ring is not suddenly torn off the liquid surface. *The weight was recorded when balance pointer was just moving towards the left and then the weight was silghtly diminished by raising up the chain, The surface tension was thus measured without actually breaking the surface and with the miuimam disturbance of the molecular arrangement of the surface.*

All the precautions necessary for obtaining accurate data were taken. For example, conductivity water was always used. The glass vessels, and the nickel basin were washed alternately with acids and alkali and finally with conductivity water and were dried inside a desiccator. Merck's pure dyestuffs were used in every case. In the case of Rhodamine B however, a small fraction of the

solid did not dissolve. Rhodamin B was therefore obtained as shining greenish crystals by crystallisation from a solution of pure alcohol.

The surface tension was calculated as follows:—

$$\text{Surface tension of the solution} = \frac{\sigma \times W_2}{W_1},$$

where σ = Surface tension of water at the temperature of the experiment.

W_2 = Weight required to raise the basin from the surface of the solution.

W_1 = Weight required to raise the basin from the surface of water.

In the case of solutions of some of the dyestuffs in water, the surface tension diminished with time, attaining a constant value after some 4 or 5 hours, depending on the nature of the dyestuff as well as on the concentration of the solution.

Results.

Table I shows the results obtained for the surface tension σ of the solutions investigated at various times t (in minutes) reckoned from the time at which the first observation was made. It will be seen that in the case of water and of aqueous solutions of Diamond fuchsin and Methylene blue, the surface tension does not change with time.

TABLE I.

Substance.	Temp.	Conc. in gm. mol. per litre.	t_1	σ	t_2	σ	t_3	σ
Pure water ...	23°	—	0	72·08	180	72·08	360	72·08
Diamond fuchsin ...	20°	0·000467	0	72·28	120	72·28		
		0·000804	0	71·73	120	71·7		
		0·00588	0	70·75	120	70·7		
Methylene blue ...	30°	0·000467	0	70·63	120	70·6		
		0·0022	0	70·6	120	70·6		
		0·0055	0	70·6	120	70·6		

In Table II, $K_{1\cdot2}$, $K_{1\cdot3}$, $K_{1\cdot4}$ are the values of K_7 (K_7 in Eqn. 8) calculated from the first and second, first and third, and first and fourth observations respectively. σ_∞ denotes the limiting value of σ usually reached after 4 or 5 hours.

TABLE II.

Substance and temp.	Conc. gm. mol. per litre.	t_1	σ	t_2	σ	t_3	σ	t_4	σ	σ_∞	$K_{1\cdot2}$	$K_{1\cdot3}$	$K_{1\cdot4}$
Crystal violet at 21°	0·00076	0	65·25	30	63·9	90	62·7	195	61·8	61·4	0·0143	0·0122	0·0115
	0·002	0	61·35	65	60	120	59·5			59·1	0·0133	0·0147	...
	0·0032	0	60·9	54	59·5	88	58·8	150	58·2	57·8	0·0117	0·0129	0·014
	0·0041	0	60·4	39	59·15	78	58·6			57·5	0·0145	0·0122	...
Rhodamine at 28°	0·00064	0	60·6	125	57·45	195	56·6		...	55	0·0056	0·0064	...
	0·00106	0	56·4	84	54·5	139	53·8		...	51·4	0·0059	0·0052	...
	0·0025	0	54·5	64	51·2	120	49·4	196	47·65	44·85	0·0071	0·0063	0·0062
	0·0074	0	45·9	49	44·5	100	43·05	225	41·8	40·9	0·0067	0·0064	0·0078
	0·0103	0	44·2	50	43·2	101	42·1	190	40·65	39·6	0·0076	0·0064	0·0078
Bismarck brown at 29°	0·0014	0	63·4	50	61·15	123	60·1	183	59·35	58·9	0·0138	0·0108	0·0124
	0·0017	0	60·65	60	59·0	130	57·9		...	57·4	0·0115	0·014	...
	0·00204	0	60·6	62	58·75	130	57·5		...	56·85	0·011	0·0133	...
	0·0033	0	58·85	50	56·95	123	55·5		...	55·1	0·0124	0·0122	...
	0·0039	0	57	62	55·8	123	55		...	54·45	0·0106	0·0128	...
Malachite green at 30°	0·00058	0	63·5	30	62·45	60	62		...	61·45	0·0233	0·0223	...
	0·00093	0	61·8	32	58	60	57·2	92	56·35	55·65	0·03	0·023	0·0235
	0·00144	0	57·6	21	56·6	62	55·45		...	55·2	0·023	0·032	...
	0·0021	0	57·4	35	55·45	67	54·75	100	54·1	53·95	0·023	0·021	0·03
	0·008	0	49·8	21	48·95		...		...	48·92	...	...	...

Discussion.

The fact that in the case of solutions of Methylene blue and fuchsine, the surface tension, as measured by the experimental method described above, did not vary with time, whereas in the case of the other solutions (Rhodamine B, Crystal violet, Bismark brown, Malachite green) there was observed a considerable diminution of surface tension with time is, in itself, a strong evidence in favour of the validity of this method for measuring variation of surface tension with time. It will be noted that the lowering of surface tension in the case of the latter group of dyestuffs, for similar concentrations is very much greater than in the case of the former group. The magnitude of this lowering is so large that these solutions may be classed with soap solutions.

When a surface of such a solution is freshly made, the surface concentration of the solute is small. The surface concentration of the micellæ increases with time until the maximum surface concentration corresponding to the particular strength of the solution is reached. The rate of condensation of micellæ on the surface from the bulk of the liquid $= K_1 C\,(1-a)$, where C is the bulk concentration and a is the fraction of surface already covered with micellæ ... (1)
The rate of removal of micellæ into the bulk of the solution from the surface $= K_2 a$ ... (2)
The rate of increase of surface concentration C of micellæ

$$\frac{dC_s}{dt} = K_1 C(1-a) - K_2 a$$

where C_s is the surface concentration of micellæ.

$$\text{or} \qquad \frac{dC_s}{dt} = K_1 C - \left[K_1 C + K_2 \right] a$$

When the volume of the solution is large, the bulk concentration C does not perceptibly change due to the ingress of micellæ into the surface. Again a may be taken as proportional to the actual surface concentration at any time. Hence

$$\frac{dC_s}{dt} = K_3 - K_4 C_s \qquad \ldots (3)$$

According to the ideas of Langmuir and Traube, the lowering of surface tension in solution

$$\sigma_o - \sigma_s = F = RTC_s \quad \ldots \quad (4)$$

where σ_o = the surface tension of the pure solvent,

σ_s = the surface tension of the solution,

F = the two dimensional gas pressure exerted by the solute molecules in excess at the interface.

Hence at a constant temperature T, $\frac{dC_s}{dt} = \frac{1}{RT} \cdot \frac{dF}{dt}$ $\left(C_s = \frac{F}{RT} \right)$

$$\text{or } \frac{1}{RT} \cdot \frac{dF}{dt} = K_3 - \frac{K_4}{Rt} F \text{ (from 3)} \quad \ldots \quad (5)$$

$$\text{or } \log_e \frac{F_\infty}{F_\infty - F} = K_6 t \quad \ldots \quad (6)$$

where F_∞ is the the value of F when $t = \infty$

$$\text{or } \frac{1}{t_2 - t_1} \log_e \frac{F\infty - Ft_1}{F\infty - Ft_2} = K_6 \quad \ldots \quad (7)$$

$$\text{or } \frac{2{\cdot}3}{t_2 - t} \log_{10} \frac{\sigma t_1 - \sigma_{t\infty}}{\sigma_{t_2} - \sigma_{t\infty}} = K_7 \quad \ldots \quad (8)$$

Where σ_{t_1}, σ_{t_2} and $\sigma_{t\infty}$ are the surface tensions of solution of constant bulk concentration at t_1, t_2 and $t\infty$ respectively.

The value of K_7 has been given as $K_{1\cdot2}$, $K_{1\cdot3}$ and $K_{1\cdot4}$ in Table II. It will be noticed that for each dyestuff the value of K_7 is within the range of experimental error, a constant, independent of the concentration of the dyestuff. This is to be expected from the theory developed above. The value of K_7 for each dyestuff is summarised in the following table.

TABLE III.

Dyestuff.	K, (mean).
Crystal violet	... 0·0133
Rhodamine B	... 0·00667
Bismarck brown	.. 0·0119
Malachite green	... 0·0253

We have thus been able to obtain a picture of the kinetic processes according to which the large molecules of the above dyes come to the surface from the bulk of the solution, and it is satisfactory to note that the quantitative equation developed on the basis of these kinetic processes, explains fairly accurately the variation of surface tension of the solutions of these organic dyes with time.

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The Photochemical Decomposition of Acetaldehyde Solution.

By J. C. Ghosh and Sunil Kumar Nandy.

Hinshelhood and Hutchison (*Proc. Roy. Soc.*, 1926, **111A**, 380) showed that the thermal decomposition of acetaldehyde vapour over the temperature range 430-592° is a homogeneous bimolecular gaseous reaction which follows the equation,

$$2CH_3{\cdot}CHO = 2CH_4 + 2CO.$$

Berthelot and Gaudechon (*Compt. rend.*, 1913, **156**, 233) made the qualitative observation that exposed to ultra-violet radiations, acetaldehyde underwent photochemical decomposition into methane and carbon monoxide. It appeared of interest to decide experimentally whether the order of photochemical decomposition in aqueous solution is the same as that of thermal decomposition. It may be mentioned that the thermal decomposition of hydrogen iodide has been found to be bimolecular, whereas the photochemical decomposition is unimolecular. As a result of this investigation, it becomes evident that the photochemical decomposition of acetaldehyde is a unimolecular reaction, while the thermal decomposition is bimolecular.

Experimental.

The source of light was a quartz mercury lamp, run at constant values of current (3 amperes) and voltage (110) from a storage battery. The acetaldehyde solution was kept inside a quartz vessel whose length was 9·8 cm. and diameter 1·6 cm. The quartz vessel had two side-tubes of very thin bore and it could be filled with liquid by placing a small funnel at one tube and applying a gentle suction at the other. The reaction tube was fixed in position in the water-bath by means of a stand and was placed at a constant distance below the light source. The temperature of the mixture was kept constant by circulating water in the bath from a thermostat by means of a pump.

The acetaldehyde solution used was very dilute and the amount of it left over was estimated with iodine and bisulphite according to the method given in Sutton's "Volumetric Analysis," p. 371.

TABLE I.

Temperature of thermostat = 27·5°.

Concentration of acetaldehyde = 0·2884*M*.

Time.	C.c. of 0·103*N*-iodine ≡3 c.c. acetaldehyde.	*k* (unimolecular).	*k* (mean).
0 min.	16·8 c.c.	—	
180	16·1	0·0002367	0·000224
360	15·6	0·0002061	

Summary of the experimental results.

Temp. of thermostat = 27·5°.

Conc. of acetaldehyde.	*k* (unimolecular).	*k* (mean).
0·2884*M*	0·0002214	
0·1301*M*	0·0002444	0·0002296
0·0685*M*	0·0002342	
0·0451*M*	0·0002185	

It will be seen that the reaction is unimolecular and the velocity constant is independent of the initial concentration of acetaldehyde solution.

Temperature coefficient of the reaction.

Temp. of thermostat.	Conc. of acetaldehyde.	*k* (unimolecular).	*k* (mean).
37·5°	0·3264*M*	0·0002944	0·0002947...(2)
,,	0·0562*M*	0·0002950	
47·5°	0·2991*M*	0·0003653	0·0003722...(3)
,,	0·0752*M*	0·0003791	

Temp. coeff. = $\frac{k_t + 10}{k_t}$ = 1·28 from (1) and (2) and = 1·26 from (2) and (3).

Quantum Efficiency of the Reaction.

For determination of the quantum efficiency, the experimental arrangement was modified, by substituting a rectangular quartz vessel 2 cm. × 2 cm. × 8 mm., with a stopper at the top. This quartz vessel was filled with acetaldehyde solution and placed behind another large quartz vessel, 4 cm. deep, through which water was circulated. This latter served as a filter. The difference in the readings of a Moll galvanometer connected with a Moll thermopile when placed immediately behind the quartz reaction cell, (*a*) filled with water and (*b*) filled with acetaldehyde solution, gave the energy of ultra-violet radiation absorbed by the acetaldehyde solution. The energy absorbed was equivalent to 0·5 Hefner at a metre. Hence number of quanta absorbed per sec., assuming $250\mu\mu$ to be the effective radiation,

$$= \frac{4 \times 900 \times 250 \times 10^{-7} \times 0{\cdot}5}{6{\cdot}5 \times 10^{-27} \times 3 \times 10^{10}} = 0{\cdot}23 \times 10^{15}$$

1 C.c. of acetaldehyde solution after two hours' exposure showed a diminution in strength equivalent to 0·2 c.c. of 0·06*M*-iodine solution. The capacity of the cell was 3 c.c.

Hence number of mols. of acetaldehyde decomposed per second

$$= \frac{3 \times 0{\cdot}2 \times 0{\cdot}06 \times 6{\cdot}16 \times 10^{23}}{1000 \times 2 \times 60 \times 60} = 3{\cdot}08 \times 10^{15}.$$

$$\text{Quantum efficiency} = \frac{\text{No. of mols.}}{\text{No. of quanta}} = \frac{3{\cdot}08 \times 10^{15}}{0{\cdot}23 \times 10^{15}} = 13{\cdot}4.$$

The value of $Nh\nu$ in this case=120,000 calories approximately. The energy required for the decomposition of one gram molecule of acetaldehyde into methane and carbon monoxide is 3,000 cal. Hence if the whole of the absorbed energy of radiation could in some way or other be transformed into the energy of chemical transformation, we should expect a maximum quantum efficiency of 40. In the decomposition of gaseous acetaldehyde by ultra-violet light, Bowen in a preliminary investigation (*J. Chem. Soc.*, 1926, **129**, 1609) found a quantum efficiency=2 approximately.

In aqueous solution the quantum efficiency is much larger than 2. Obviously a chain reaction is set up. The fact that there is

a definite, though small, temperature coefficient of the velocity of reaction, also supports the idea that a reaction chain is set up. We may assume the following stages:—

$$CH_3{\cdot}CHO + h\nu \longrightarrow CH_3{\cdot}CHO \text{ (excited)} \ldots\ldots (1)$$

$$CH_3{\cdot}CHO \text{ (excited)} + CH_3{\cdot}CHO \longrightarrow CH_4 + CO + CH_3{\cdot}CHO \text{ (lower stage of excitation.)} \quad \ldots\ldots (2)$$

If the velocity of reaction (2) is small compared with the reverse reaction in (1), as is very possibly the case, the concentration of the excited molecules of acetaldehyde will be proportional to the absorbed energy of radiation. Molecular extinction coefficients of acetaldehyde in the region $280\mu\mu - 230\mu\mu$ have been determined in this laboratory and the values have been found to be very large. Hence we are justified in assuming that the whole of the incident effective radiation is absorbed by even very dilute solutions of acetaldehyde, and that the amount of energy absorbed does not vary with the concentration of the acetaldehyde solution. The velocity of reaction is therefore given by

$$\frac{dx}{dt} = kIC \text{ (acetaldehyde)} \qquad \text{from (2)}$$

where I is the intensity of incident radiation, and we obtain a unimolecular constant.

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The Reduction of *o*-Nitrotoluene.

By P. S. Varma and V. Anna Rao.

The reduction of *o*-nitrotoluene does not seem to have been so systematically studied as the reduction of other nitro-hydrocarbons of the aromatic series. Petrieff (*Ber.*, 1873, **6**, 557) and Goldschmidt (*Ber.*, 1878, **11**, 1624) seem to be the earliest workers who appear to have obtained a tolidine from *o*-nitrotoluene through hydrazotoluene. Klinger (*Ber.*, 1882, **15**, 865) obtained by the action of sodium methylate on *o*-nitrotoluene red amorphous bodies, none of which he could purify and identify. Haeussermann (*Chem. Zeit.*, 1893, **17**, 129, 209) carried on the electrolytic reduction of *o*-nitrotoluene in alcoholic solution (6-8 amperes, 6 volts) and obtained hydrazotoluene first and tolidine later on at the cathode. Evans and Fry (*J. Amer. Chem. Soc.*, 1904, **26**, 1161) reduced *o*-nitrotoluene by means of magnesium amalgam and obtained a 50 per cent. yield of *o*-azoxytoluene in the presence of ethyl alcohol and a 66·5 per cent. yield of *o*-azotoluene in the presence of methyl alcohol. van Loon (*Chem. Weekblad*, 1908, **5**, 689) mentions to have obtained a good yield of tolidine from hydrazotoluene. While studying the action of the Grignard's reagent on aromatic nitro-compounds, Hepworth (*J. Chem. Soc.*, 1920, **117**, 1004), obtained ethyl- (or methyl)-*o*-toluidine and 2:2-azotoluene by means of magnesium powder and ethyl (or methyl) bromide. Zechmeister and Rom (*Ber.*, 1926, **59**, 867) obtained the azoxy-derivative by reducing *o*-nitrotoluene by means of magnesium turnings in presence of a large quantity of methyl alcohol and a saturated aqueous solution of ammonium chloride.

It will thus be seen that no systematic work has been carried out on the reduction of *o*-nitrotoluene. It was therefore thought desirable to investigate the subject thoroughly and find out the exact

conditions under which different reduction products could be obtained by using different reducing agents.

The present paper includes the results obtained by using various reducing agents such as sodium methylate, sodium ethylate, alcoholic potash, magnesium powder, aluminium dust, zinc dust, hydrogen sulphide in alcoholic ammoniacal solution, sodium arsenite, zinc and ammonium chloride solution in presence of alcohol, sulphides of heavy metals in alkaline solutions, iron in presence of sodium chloride solution, sodium disulphide, stannous chloride in an alkaline or in an acid solution and tin and hydrochloric acid. By using these reducing agents under different conditions *o*-azoxytoluene, *o*-azotoluene, *o*-hydrazotoluene and *o*-toluidine have been obtained.

o-Azoxytoluene has been obtained in more or less yield by means of magnesium powder in presence of methyl or ethyl alcohol and ammonium chloride solution, zinc dust or aluminium dust or stannous chloride in alkaline solutions and hydrogen sulphide in alcoholic ammoniacal solutions. A better yield is, however, obtained by means of zinc dust in presence of ammonium chloride solution at 100°.

o-Azotoluene is the main product when *o*-nitrotoluene is reduced by means of sodium methoxide or ethoxide at 100° or by means of aluminium wire (or dust) or zinc dust and caustic soda solution at 100°. By reduction with stannous chloride in an alkaline solution some azo-compound along with azoxy-compound is obtained. By reducing azoxytoluene by means of zinc dust or phosphorus pentachloride, azotoluene is also obtained.

o-Hydrazotoluene is obtained along with *o*-azotoluene when aluminium or zinc dust in an alkaline solution is used. This compound is also obtained when *o*-azotoluene is reduced by means of alcoholic ammonium sulphide.

Small quantities of *o*-toluidine are found in the end products when reduction is carried on by sodium methoxide, sodium ethoxide or aluminium dust in caustic soda solution. A fairly good yield of *o*-toluidine is obtained by reduction with sodium disulphide, or by stannous chloride in an acid solution, or by tin and hydrochloric acid.

No reduction product has been obtained by sodium arsenite, or by the sulphides of heavy metals in an alkaline solution or by iron and sodium chloride solution or by means of benzoin.

Experimental.

Reduction of o-Nitrotoluene to o-Azoxytoluene.

1. *By means of magnesium powder.* The reducing action of magnesium powder on *o*-nitrotoluene in presence of methyl or ethyl alcohol and a saturated aqueous solution of ammonium chloride has been studied in a series of experiments (see Table I) to find out the exact conditions under which the maximum yield of the reduction product may be obtained. The experiment has usually been carried out by taking *o*-nitrotoluene (12 g.), adding to it methyl or ethyl alcohol (150 c.c.) and a saturated solution of ammonium chloride or other salts (150 c.c.) and then a certain quantity of magnesium powder and heating the mixture on a water-bath in a flask provided with an upright condenser for 6 to 7 hours. At the end of the reaction, the product is filtered while still hot, the alcohol distilled off and the residue treated with excess of water. It is again filtered and the residue is extracted with alcohol and crystallised. The product in most cases has been found to melt sharply at 58·5° and identified to be *o*-azoxytoluene.

The experiment of Zechmeister and Rom (*loc. cit.*) has been repeated but we could not obtain the same yield as claimed by the authors. It has been possible, however, to get a much larger yield by changing the proportions of the reagents used. Methyl and ethyl alcohols have been tried and a proportionately larger yield of the *o*-azoxy-compound has been obtained in the case of ethyl alcohol. In place of ammonium chloride, other compounds such as sodium chloride, aluminium chloride and ammonium sulphate have also been used. Sodium and aluminium chlorides are quite ineffective whilst ammonium sulphate has been found to yield a certain quantity of the azoxy-compound. From this it seems that the ammonium radicle is responsible for the catalytic action and not the chloride ion.

2. *By means of zinc dust in a neutral medium.* Experiments similar to the above have been carried on with the only difference that zinc dust has been used in place of magnesium powder. *o*-Azoxytoluene has been obtained in this case also but the yield is very small. Zinc dust is therefore found to be not so effective a reducing agent as magnesium powder under similar conditions.

3. *By means of zinc dust in an alkaline medium.* *o*-Nitrotoluene (12 g.) and ethyl alcohol (150 c.c.) are put in a flask provided with an upright condenser. Zinc dust (25 g.) is added to it and then a 30 per cent. sodium hydroxide solution (200 c.c.). The reaction is allowed to proceed at the room temperature for one hour. It is then gently warmed for a short time in a water-bath and filtered while still hot. The alcohol in the filtrate is distilled off and the residue filtered off and washed with water. It is dried and extracted with alcohol and crystallised. Thus pure *o*-azoxytoluene (3·6 gm.) is obtained.

4. *By means of aluminium wire in an alkaline medium.* Experiment similar to (3) is carried on with aluminium wire in place of zinc dust. The yield of the azoxy-derivative is still poor, being about 20 per cent.

5. *By means of stannous chloride in an alkaline medium.* *o*-Nitrotoluene (12 g.) is taken in a flask provided with an upright condenser and a 30 per cent. sodium hydroxide solution (50 c.c.) is added. Alcohol (150 c.c.) together with stannous chloride (15 g.) are also added and the mixture is heated on a water-bath for about 4 hours. The alcohol is then distilled off, the residual product treated with dilute hydrochloric acid to remove the alkali, and filtered. The residue on the filter-paper is dried, extracted with hot absolute alcohol and crystallised. *o*-Azoxytoluene (about 4·5 g.) is obtained. The experiment has been repeated with 20, 25 and 30 g. respectively of stannous chloride but no change is observed either in the quantity or the nature of the product obtained. It has been found, however, that if the duration of reaction is increased to eight hours when 15 gm. of stannous chloride are taken, 4 gm. of *o*-azoxytoluene and 2·5 gm. of *o*-azotoluene are obtained. The reduction of *o*-nitrotoluene by means of stannous chloride in alkaline medium to the amino-compound is not effected as in the case of nitrobenzene.

6. *By means of hydrogen sulphide in an ammoniacal medium.* Attempts have been made to reduce *o*-nitrotoluene by means of hydrogen sulphide at the ordinary temperature in presence of ammonia and alcohol. With 12 gm. of *o*-nitrotoluene, only 0·8 gm. of *o*-azoxytoluene is obtained after two hours and the reduction does not proceed further to any appreciable extent. No improvement in the yield was observed on conducting the experiment at 60°.

TABLE I.

o-Nitrotoluene taken = 12 gm.

Expt.	Reducing agent (gm.).	Methyl or ethyl alcohol (c.c.).	Medium : a saturated solution (c.c.).	Percentage yield of *o*-azoxytoluene.
	Magnesium	*Methyl alcohol*	*Ammonium chloride*	
1	6	150	150	35·4
2	10	,,	,,	62·7
3	12	,,	,,	66·6
4	15	,,	,,	88·7
		Ethyl alcohol		
5	6	150	,,	42·4
6	8	,,	,,	65·7
7	12	,,	,,	72·7
			Sodium chloride	
8	,,	,,	150	Very little.
			Aluminium chloride	
9	,,	,,	150	Nil.
			Ammonium sulphate	
10	,,	,,	150	48·5
	Zinc		*Ammonium chloride*	
11	12	,,	150	12·3
12	16	,,		13·4
			Sodium hydroxide	
13	25	,,	200 (30%)	36·4
	Aluminium			
14	5	5	,,	20·2
	Stannous chlotide			
15	15	,,	100	45·5
16	20	,,	,,	55·6
17	*Hydrogen sulphide*	,,	*Ammoniacal*	8·1

Remarks.—In expts. 1-14 heating on a water-bath was continued for 6-7 hours. In expts. 15 and 16, the duration of heating was 4 hours. Expt. 17 was conducted at room temp. for one hour.

Reduction of o-Nitrotoluene to o-Azotoluene.

7. *Reduction by means of sodium methoxide.* Sodium is dissolved in an excess of methyl alcohol and the solution is added to *o*-nitrotoluene in a flask provided with an upright condenser and heated on a water-bath for 8 hours. The excess of methyl alcohol is then distilled off. The product is then shaken with a large excess of water to dissolve out the sodium formate formed in the reaction and filtered. The residue is purified by repeated crystallisation from ether. The product so obtained forms red monoclinic crystals and is identified to be *o*-azotoluene, m.p. 50°.

Different experiments have been done by using different quantities of sodium, keeping the amounts of *o*-nitrotoluene and methyl alcohol the same. It has been found that the maximum yield of *o*-azotoluene is obtained when 5 gms. of sodium are used and that by increasing the quantity of metallic sodium the yield of the azo-compound decreases with the corresponding increase of that of toluidine. The reaction mixture is heated for four or eight hours. The duration of heating has no appreciable change in the yield of the azotoluene. Along with *o*-azotoluene in all these experiments small quantities of *o*-azoxytoluene, *o*-toluidine, some resinous products and a small quantity of unaltered *o*-nitrotoluene have been obtained.

8. *Reduction by means of sodium ethylate.* In a few experiments sodium ethylate has been used in place of sodium methylate under similar conditions but with no better result. Here also small quantities of *o*-azoxytoluene, *o*-toluidine and some resinous products are obtained.

9. *Reduction by means of aluminium wire (or dust) and sodium hydroxide at* 100°. A series of experiments have been carried out using aluminium dust as a reducing agent in alkaline solutions. *o*-Nitrotoluene (6 g.) and methyl alcohol (150 c.c.) are put in a flask provided with a reflux condenser. A definite quantity of aluminium is then added and then a definite quantity of sodium hydroxide solution is dropped (5 c.c. at a time) from the top of the condenser at an interval of two minutes. The reaction is vigorous and the flask has therefore to be cooled from time to time to prevent the reaction from becoming too violent. When the whole of the sodium hydroxide solution has been added and the reaction slackened, the reaction product is heated on a water-bath for 8 hours. The product is then distilled to remove the alcohol and the solution

neutralised by means of dilute hydrochloric acid. The insoluble residue is removed by filtration and extracted by means of absolute alcohol. The alcoholic extract gave crystals which were recrystallised from the same solvent. *o*-Azotoluene and *o*-hydrazotoluene are separated by means of fractional crystallisation from alcohol. A very small quantity of *o*-toluidine has also been found in the product. A number of such experiments have been done using different amounts of aluminium dust and sodium hydroxide from which it is clear that a mixture of *o*-azotoluene and *o*-hydrazotoluene is always obtained. By increasing the quantity of aluminium dust or of sodium hydroxide solution there has been an almost proportionate increase in the yield of the products.

It is interesting to find that by using aluminium in the form of wire *o*-azotoluene only is obtained.

10. *Reduction by means of zinc dust in an alkaline medium.* The experimental details here are the same as in the case of aluminium dust. A very good yield of *o*-azotoluene (about 87 per cent.) is obtained by using 10 gm. of zinc dust and 30 gm. of caustic soda in 100 c.c. solution with 6 gms. of *o*-nitrotoluene. By increasing either the amount of zinc dust or of caustic soda, no appreciable change in the yield is observed.

11. *Reduction by means of stannous chloride in an alkaline solution.* The experimental details are mentioned under the formation of azoxytoluene. By using this reagent a certain quantity of *o*-azotoluene (about 62 per cent. of the total yield) is always obtained along with *o*-azoxytoluene. It has not been possible to get this product exclusively by increasing the quantity of the reducing agent.

12. *Reduction of o-azoxytoluene to o-azotoluene by means of iron dust.* By gently heating *o*-azoxytoluene directly over flame with iron dust in a tube, it has been possible to get some azotoluene condensed on the cooler parts of the tube but the yield is poor and other products, such as *o*-toluidine, have also been obtained in small quantities.

13. *Reduction of o-azoxytoluene to o-azotoluene by means of phosphorus pentachloride.* A better yield of *o*-azotoluene from *o*-azoxytoluene is, however, obtained by reduction with phosphorus pentachloride. *o*-Azoxytoluene (5 g.) is heated on a water-bath at 60°. Phosphorus pentachloride (about 3 g.) is then added. A vigorous reaction follows. When it has subsided, the products are washed with water to remove the excess of phosphorus pentachloride and

phosphorus oxychloride formed in the reaction. The solid residue is then dried and crystallised from absolute alcohol and thus pure azotoluene (2·5 g.) is obtained.

TABLE II*a*.

o-Nitrotoluene taken = 6 gm.

Expt.	Metallic sodium (gms.)	Methyl or ethyl alcohol	Time allowed for the reaction.	Percentage yield of azo-toluene.
		Methyl alcohol.		
1	4	100 c.c.	4 hrs.	39·2
2	5	,,	,,	47·9
3	4	,,	8	39·2
4	5	,,	,,	47·9
5	8	,,	,,	39·2
6	10	,,	,,	33·1
		Ethyl alcohol		
7	5	100 c. c.	4	47·9
8	8	,,	,,	34·8

TABLE II*b*.

o-Nitrotoluene taken = 6 gm. Ethyl alcohol = 150 c.c.

Expt.	Reducing agent (gm.)	Sodium hydroxide.	Percentage yield of azo-compd.	Remarks.
	Aluminium dust			
1	7·5	30 g. in 100 c.c.	8·2	Main product—hydrazotoluene in expts. 1—3.
2	12·5	30 ,, ,,	10·9	
3	7·5	50 ,, ,,	10·9	
	Aluminium wire			
4	7·5	30 ,, ,,	43·5	
	Zinc dust			
5	10	30 ,, ,,	87·0	
6	15	30 ,, ,,	87·0	
7	7·5	30 ,, ,,	83·4	
8	7·5	40 ,, ,,	78·3	
9	10·0	3 ,, ,,	65·2 (azo) 13·1 (hydrazo)	Heated for 8 hrs.
	Stannous chloride			
10	7·5	15 ,, ,,	40·4 (azo) 21·1 (hydrazo)	

Reduction of o-*Nitrotoluene to* o-*Hydrazotoluene.*

14. *By means of aluminium dust in an alkaline solution.* The experimental details are given under reduction of *o*-nitrotoluene to *o*-azotoluene. A mixture of azo- and hydrazo-toluenes is always obtained by this method. Attempts to get exclusively only one product have failed. The maximum yield, about 47 per cent. is obtained by using 12·5 g. of aluminium dust and 30 g. of caustic soda for 6 g. of *o*-nitrotoluene.

15. *By means of zinc dust in an alkaline solution.* The experimental details are given under the reduction of *o*-nitrotoluene to *o*-azotoluene. The yield is still poor, being only about 13 per cent.

16*a*. *Reduction of* o-*azotoluene to* o-*hydrazotoluene.* A better yield of *o*-hydrazotoluene (about 75%), is obtained by reducing *o*-azotoluene by means of alcoholic ammonium sulphide. *o*-Azotoluene is dissolved in alcohol and excess of ammonium sulphide added and the reacting mixture allowed to stand for six hours. A solid separates out. If the mixture is kept at a higher temperature, the reaction seems to proceed more quickly.

16*b*. A still better yield of *o*-hydrazotoluene (about 95%) is obtained if ammonia is added to a solution of *o*-azotoluene in alcohol and a steady current of hydrogen sulphide is passed for about one hour.

TABLE III.

Expt.	Substance to be reduced (in gm.).	Reducing agent (in gm.).	Sodium hydroxide (in gm. in 100 c.c.).	Methyl-alcohol (in c.c.).	Time allowed for the reaction.	Percentage yield of hydrazotoluene.
	o-Nitrotoluene	*Aluminium*				
1	6	7·5	30	150	6 hrs. on W.B.	34·5
2	,,	12·5	,,	,,	,, ,,	45·2
3	,,	7·5	50	,,	,, ,,	38·8
4	,,	10	30	,,	8 ,,	12·9
	Azotoluene					
5	4	*Ammonium sulphide*	—	100	6 hrs. at room temp.	74·2
6	4	H_2S	—	,,	1 ,, ,,	94

Reduction of o-Nitrotoluene to o-Toluidine.

Small quantities of *o*-toluidine are obtained in the products when sodium methoxide, sodium ethoxide and aluminium dust are used as reducing agents. A better yield of *o*-toluidine (about 70%) is obtained when *o*-nitrotoluene is reduced by means of sodium disulphide. This reagent is prepared by adding sulphur to a boiling aqueous solution of sodium sulphide till it dissolves no more of sulphur. *o*-Nitrotoluene (10 g.) is taken in a flask provided with an upright condenser, alcohol (100 c. c.) and sodium disulphide solution are added and the mixture is heated on a water-bath for 3 to 4 hours. The alcohol is then distilled off. A layer of *o*-nitrotoluene and *o*-toluidine separates out. They are separated by steam distillation.

A still better yield (about 83%) is obtained by reducing *o*-nitrotoluene by means of tin and hydrochloric acid. Here the process is the same as in the case of nitrobenzene.

o-Toluidine has also been obtained in fairly a good yield (80%) by reducing *o*-azotoluene by means of stannous chloride in an acid medium. Here *o*-azotoluene (6 g.) is taken in a flask provided with a reflux condenser and stannous chloride (10 g.) in hydrochloric acid (35-40 c. c.) is added. Alcohol (100 c. c.) is then added to it and the reaction mixture heated on a water-bath for 3 to 4 hours. After removal of alcohol, the residue is treated with water, and *o*-toluidine separated.

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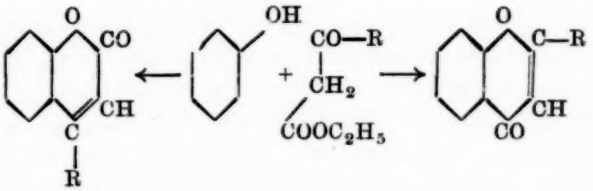
Synthesis of Tetrahydroxanthones.

By Manmohan Sen.

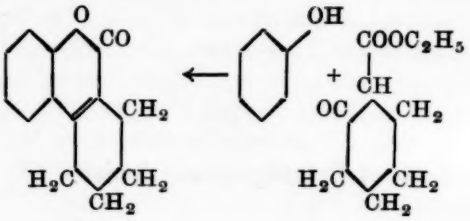
In the condensation of β-ketenic esters with phenols there are two possible courses, one leading to the formation of coumarins (Pechmann's reaction) and the other to chromones (Simonis' reac-



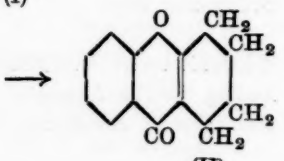
tion). The work of Baker and Robinson (*J. Chem. Soc.*, 1925, **127**, 1981, 2349) and of Bargellini (*Gazzetta*, 1925, **55**, 945) clearly prove that under Pechmann's conditions the condensation, contrary to the claims of Jacobsen and Ghosh, leads to coumarins irrespective of the nature of the β-ketonic ester employed.

Sen and Basu (*J. Indian Chem. Soc.*, 1928, **5**, 467) condensed ethyl *cyclo*hexanone-2-carboxylate with phenols to note if a cyclic β-ketonic ester (in which the reactive methine group is situated in the nucleus) have any influence in changing the course of the reaction. The products exhibited extraordinary stability towards alkalis and Sen and Basu were uncertain at first if these were coumarins (I) or chromones (II). They decided ultimately in favour of the coumarin structure as 2-cyano*cyclo*hexanone gave identical products. Sonn (*Ber.*, 1918, **51**, 1829) and Bargellini and Forli-Forti (*Gazzetta*, 1911, **41**, 747) observed that cyano-ketones of the

types $CN{\cdot}CH_2{\cdot}CO{\cdot}R$ on condensation with phenols invariably yield coumarins and not chromones.



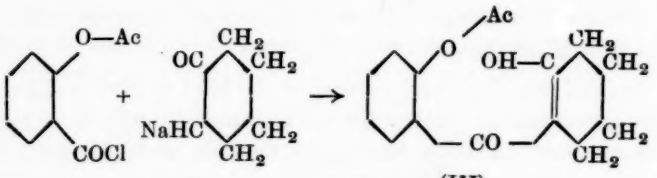
(I)



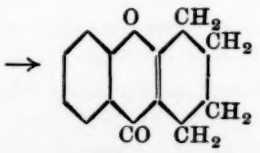
(II).

In view of this there could not be left any doubt about the coumarin structure (I) assigned by Sen and Basu. It was thought however that conclusive evidence would be obtained by the synthesis of the corresponding tetrahydroxanthones (II).

Initial efforts to condense ethyl *o*-methoxybenzoate with *cyclo*hexanone by means of sodium gave unsatisfactory results. It may be mentioned that Edouard Bauer (*Ann. Chim.*, 1914, (*ix*), **1**, 393) obtained benzoyl *cyclo*hexanone in very poor yield from ethyl benzoate and *cyclo*hexanone. The condensation succeeded better with *o*-acetoxy benzoyl chlorides and sodio-*cyclo*hexanones.



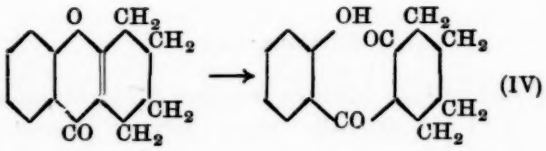
(III)



(II).

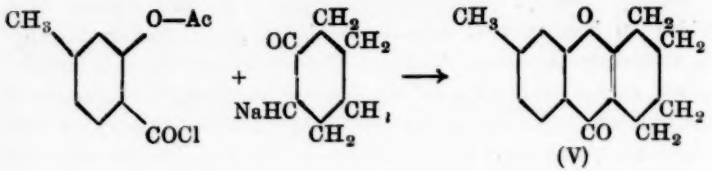
o-Acetoxy benzoyl *cyclo*hexanones (III) were first formed from which on heating with concentrated hydrochloric acid the tetrahydroxanthones (II) were obtained. This method follows an unambiguous course and leaves no doubt about the xanthone structure of the products. The yields however were not satisfactory as side reactions, particularly the formation of diacyl*cyclo*hexanones, took place and the unaltered *cyclo*hexanones (specially *p*-methyl*cyclo*hexanone which is insoluble in water) greatly hindered the isolation of the products in the solid form. Different procedures were therefore followed with *cyclo*hexanone and *p*-methyl*cyclo*hexanone in isolating the products.

Reduced xanthones had not been described before and the tetrahydroxanthones obtained here are the only representatives of the class. While xanthones have high melting points these reduced bodies are quite low melting. They are crystalline substances and are extremely soluble in all organic solvents excepting ligroin. They do not form, like xanthones and chromones, oxonium salts. Even perchlorates could not be isolated though perchloric acid is the most useful reagent for obtaining stable salts of weak bases. (Hofmann, *Ber.*, 1910, **43**, 178). The non-formation of oxonium salts is due obviously to the presence of the reduced ring. The influence of reduced rings on the basic character of oxygen has been amply demonstrated by the work of Ghosh (*J. Chem. Soc.*, 1915, **107**, 1588). The tetrahydroxanthones were readily hydrolysed by alkalis to *o*-hydroxy acids and *cyclo*hexanones, so much so that the intermediate *o*-hydroxy benzoyl *cyclo*hexanones (IV) could not be isolated.

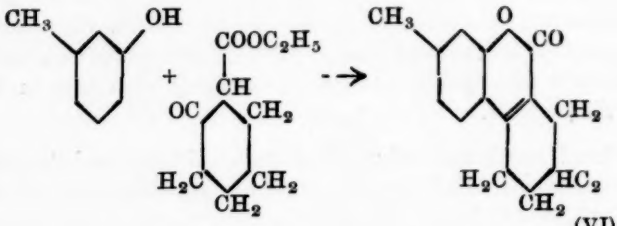


(IV)

7-Methyltetrahydroxanthone (V) was synthesised from acetyl *m*-cresotyl chloride and sodio*cyclo*hexanone. It melted at 110°. Sen and Basu's compound from *m*-cresol and *cyclo*hexanone-2-carboxylate had m.p. 119° and therefore could only be (VI).



(V)



(VI).

This proves conclusively that the products obtained by Sen and Basu are really coumarins (I) and not chromones (II). Hence cyclic β-ketonic esters also condense with phenols in the usual manner. This establishes beyond dispute the general character of Pechmann's reaction and shows that in the condensation of β-ketonic esters with phenols the course of the reaction depends entirely on the nature of the condensing agent and is quite independent of the nature of the β-ketonic esters employed. Coumarins readily dissolve in alkalis on warming by the opening up of the lactonic ring. The peculiar stability of the coumarins of Sen and Basu therefore must be due to the presence of the reduced benzene ring, fused in 3 : 4-position of the coumarins.

Experimental.

Tetrahydroxanthone.—Molecular sodium (0·7 g.) suspended in dry ether (40 c.c.) was gradually treated with an ethereal solution (10 c.c.) of *cyclo*hexanone (3 g.). The sodium gradually disappeared and the sodium salt of *cyclo*hexanone separated out. When the reaction was over, the flask was cooled with ice and acetyl salicylyl chloride (6 g.) dissolved in ether (20 c.c.) was slowly introduced. After refluxing on the water-bath for 6 hours, cold dilute hydrochloric acid was added and the ethereal layer thoroughly washed with dilute sodium carbonate solution. On evaporating off the ether

a heavy oil was obtained which was boiled with concentrated hydrochloric acid for an hour. The oily product was taken up in ether and washed with dilute alkali. On removing the ether a solid crystalline mass contaminated with some oil was obtained. It was dried on a porous plate and crystallised from petrol ether. Tetrahydroxanthone was obtained as rhombic cubes, m.p. 105°. It is very soluble in alcohol, benzene, ethyl acetate, acetone and ether, fairly soluble in benzine, and less so in petrol ether. It does not form a hydrochloride. Efforts at obtaining the perchlorate also gave no positive results. (Found: C, 77·87; H, 6·21. $C_{13}H_{12}O_2$ requires C, 78·00; H, 6·0 per cent.

6-*Methyltetrahydroxanthone*.—Sodio*cyclo*hexanone (from 0·7 g. sodium and 3 g. *cyclo*hexanone) was condensed as above with acetyl *p*-cresotyl chloride (6 g.) to form 6-methyltetrahydroxanthone. It crystallised from ligroin in elongated needles, m.p. 113°. Its solubility in different organic solvents resembled that of the previous compound. (Found: C, 78·38; H, 6·72. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·54 per cent.).

7-*Methyltetrahydroxanthone* was prepared as before from sodio*cyclo*hexanone and acetyl *m*-cresotyl chloride. On purification from petrol ether thin scales, m.p. 100° were deposited. (Found: C, 78·41; H, 6·66. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·54 per cent.).

3-*Methyltetrahydroxanthone*.—To an ethereal suspension of sodio*cyclo*hexanone (from 7 g. sodium and 3·4 g. of the ketone) an ethereal solution of acetyl salicylyl chloride (6 g.) was added gradually with ice-cooling. After heating on the water-bath for six hours the intermediate compound was extracted out with dilute caustic soda solution and precipitated from the alkaline solution with ice-cold dilute acetic acid as a thick oil. This was heated with concentrated hydrochloric acid for an hour. The oily product was washed in ethereal solution with cold dilute alkali when it was obtained as a semi-solid mass on evaporation of the ether. After drying on a porous plate it was crystallised from petrol ether, rectangular plates, m.p. 130-131° being deposited. (Found: C, 78·33; H, 6·81. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·54 per cent.).

3:6-*Dimethyltetrahydroxanthone*.—Sodio-*p*-methyl*cyclo*-hexanone and acetyl *p*-cresotyl chloride gave 3:6-dimethyltetrahydroxanthone, which separated from petrol ether as needles, m.p. 137-138°.

(Found: C, 79·09; H, 7·28. $C_{15}H_{16}O_2$ requires C, 78·95; H, 7·00 per cent.).

3:7-*Dimethyltetrahydroxanthone* was obtained from sodio-*p*-methyl *cyclo*hexanone and acetyl *m*-cresotyl chloride and recrystallised from ligroin. M.p. 118-119°. (Found: C, 78·81; H, 7·23. $C_{15}H_{16}O_2$ requires C, 78·95; H, 7·00 per cent.).

My grateful thanks are due to Prof. P. C. Mitter, M.A., Ph.D. for his kind interest in the work throughout.

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Reactions at the Surface of Hot Metallic Filaments. Part I. The Reaction $CO_2 + H_2 \rightarrow H_2O + CO$ on Platinum.

By B. S. Srikantan.

Prichard and Hinshelwood (*J. Chem. Soc.*, 1925, **127**, 806) have studied the reaction between carbon dioxide and hydrogen in the presence of a hot platinum wire and have shown that carbon monoxide and water are formed and that the reaction proceeds to completion on absorption of the water. The temperature of the wire was known from its resistance, which according to them was controlled in such a way that the reaction velocities were reproducible to 1 per cent. The data for the reaction-time given by them (*loc. cit.*, p. 808) yield good velocity constants (by the usual unimolecular formula) except for the first value, which is about 25 per cent. in excess of the mean value of the rest. Again a careful examination of the data represented graphically in Figs. 2 and 3 of their paper, shows that their results are not quite so reproducible as they claim. For example in Fig. 2, Curve II of their paper with 100 mm. of each of carbon dioxide and hydrogen at 1090° and after 300 sec., 20 mm. of carbon monoxide are formed, while according to Curve III, 49 mm. of carbon monoxide are obtained and in Fig. 3, Curve II, a similar experiment gives 30 mm. of carbon monoxide. Again in Fig. 3, Curve I, with 50 mm. of hydrogen and 100 mm. of carbon dioxide at 1000° after 300 sec., 25 mm. of carbon monoxide are formed whereas a similar experiment in Fig. 2, Curve II, gives only 10 mm.

It appears therefore, that there is a drift in the activity of the wire and every time an experiment is performed, the condition of the surface is not the same as in the previous instance. Further it is possible that a part of this discrepancy could be attributed to an inefficient method of temperature control.

An attempt has been made in this investigation to secure a more efficient temperature control than the previous workers and the kinetics of the reaction has been studied with the idea of noting the drift in the activity of the wire, due to any change in the surface, during the reactions. The experiments are described in the order

in which they were performed, giving a continuous history of the wire.

The present paper forms a part of an investigation undertaken with the object of studying the effect of various surfaces like platinum, platinum-iridium alloys, tungsten and thoriated tungsten on the interaction of carbon dioxide and hydrogen.

The Apparatus.

The apparatus (Fig. 1) consists of a cylindrical vessel which is closed by a ground glass top and made air-tight by securing with a cement of bees-wax and rosin. The catalyst wire (about 24 cm. long and 0·01 cm. in diameter), directly welded on to stout copper leads, is hung inside the vessel in the form of a U. The bottom of the vessel contains phosphorus pentoxide to absorb the water formed during the reaction and thus cause the reaction to proceed to completion. The connections to the pump and the manometer were all made of capillary tubes.

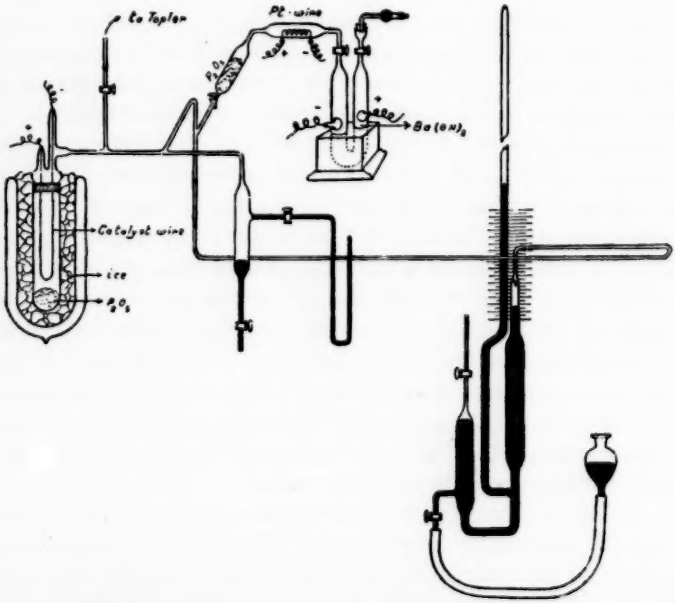


Fig. 1.

Temperature Control.

Prichard and Hinshelwood (*loc. cit.*) measured the resistance of the hot wire with an ammeter in series and a voltmeter in parallel and from the resistance and the temperature coefficiet of the resistance of the wire, they calculated its temperature. They allowed a rough correction of 5 per cent. for the unheated portion of the wire passing through the seal. But it was found in the course of the experiments described here, that the temperature could not be controlled to any degree of accuracy, by an ammeter and a voltmeter alone. The wire was heated by means of a 110-volt battery with a resistance in series. As the reaction proceeded the resistance of the wire increased and the volt and ammeters altered their readings; while the wire was seen to rise from dull red heat to a bright glow.

So the catalyst wire was made one arm of a Wheatstone's bridge and balanced against a known resistance. The ratio of the constant arms was 10 : 1. By changing the variable arm in a suitable manner the resistance of the wire could be also changed. Volt-ammeter readings were used to calculate the temperature of the wire.

To calculate the temperature of the wire from its resistance, the temperature coefficients of the resistance of the wire between the melting point of ice and the temperature of steam was determined carefully. The resistance of the wire for various currents from 0·05 to 0·175 amp. was measured at the two temperatures, with the aid of a platinum thermometer bridge, with compensating leads of about 1·6 cm. in the circuit, in order to allow for the cooling effect at the leads while the wire was heated. The resistances of the wire for zero current at these temperatures were obtained from the graph (current-resistance) by extrapolation. The following table gives the data for the temperature coefficient of the resistance of three samples of wires used in this investigation.

TABLE I.

Wire.	Temp. coeff. of resistance (α).
No. 1	$38{\cdot}7 \times 10^{-4}$
No. 2	$37{\cdot}5 \times 10^{-4}$
No. 3	$38{\cdot}3 \times 10^{-4}$

Method of Experiment.

Carbon dioxide prepared from pure dry magnesium carbonate and dried over phosphorus pentoxide was collected over mercury in small sampling tubes. Hydrogen was prepared by the electrolysis of a 10 per cent. solution of baryta (Fig. 1). The apparatus was first exhausted and the reaction vessel was immersed in melting ice in an unsilvered Dewar vessel. Carbon dioxide was then let into the apparatus at known pressures from the sampling tubes. Hydrogen from the electrolytic cell was slowly led over a glowing spiral of platinum (to remove the last traces of oxygen) and dried over a long column of phosphorus pentoxide and finally let into the apparatus. Before noting the pressures, the manometer was always adjusted to a constant level. Thus the pressure of each of these gases at constant volume and at 0° was noted. Since the connections to the topler and the manometer were all made of capillary tubes, the effect of the dead space was negligible especially as the volume of the reaction vessel was above 250 c.c.

The current was switched on for a suitable period, measured by a stop watch. Meanwhile care was taken to balance the bridge. After cutting off the current the wire and the gases were allowed to cool; the water formed was absorbed by the phosphorus pentoxide and the pressure at constant volume was noted. The change in the pressure gave a measure of the reaction velocity. By a repetition of this process the reaction was followed to the end. Thus all the measurements were made at 0° and at constant volume.

In all these experiments it was noticed that the catalyst wire was not steady in activity. It was extremely difficult to get reproducible values at first. After prolonged working the values were fairly reproducible.

Reaction Velocity.

Prichard and Hinshelwood (*loc. cit.*) assume the amount of carbon monoxide formed in the first 300 sec. as a measure of the reaction rate. But it is evident from the results presented here and from their data quoted before that such a procedure is not justifiable. The reaction starts with a high velocity and rapidly falls to a low and steady value. The results are given in the following tables.

With the fresh wire the velocity coefficients calculated on the basis of the usual unimolecular formula, fall off rapidly (Table II). Subsequent experiments show (Tables III and III*a*) that the wire reaches a steady state and unimolecular constants are obtained except for the initial stages. In the next set of experiments (Table IV), the wire was heated to about 1000° in a vacuum for 2 minutes between any two experiments in order to expel any of the adsorbed carbon monoxide. Such a treatment was found to have deactivated the catalyst to a considerable extent. The reaction did not proceed to completion at 1011° but went to about 15 per cent. in 90 sec., and stopped. This 15 per cent. conversion is somewhat like the initial rapid reaction rate. But the wire was able to catalyse the reaction at a higher temperature (Table IV). The results were fairly reproducible after heating the wire in vacuum between experiments.

In Tables III, III*a*, and IV the velocity coefficients are constant after a preliminary period, during which they fall off rapidly.

TABLE II.

Fresh wire No. 1.

P_{CO_2} = 100 mm. P_{H_2} = 100 mm. Temp. = 1011°.

Time	Total pressure.	R*	$(1/c+a)$**
0 sec.	200·0 mm.	—	—
60	164·0	0·00744	900
510	158·0	0·00106	900
1120	153·5	0·000557	900
1500	149·0	0·000474	900
1900	146·0	0·000407	900
2300	142·5	0·000370	910
2700	140·5	0·000334	910
3600	135·5	0·000287	910
4800	130·5	0·000246	—
			Mean 904

* R in this and the following tables represents the velocity coefficients calculated with the usual unimolecular formula.

** The last column in this and other tables $(1/c+a)$ will be explained in the next section dealing with the initial stages of the reaction.

TABLE III.

P_{CO_2} = 103 mm. P_{H_2} = 100 mm. Temp. = 1011°.

Time.	Total pressure.	R.	$(1/c+a)$.
0 sec.	200·0 mm.	—	—
60	192·0	0·00138	98
300	188·0	0·00043	100
900	180·0	0·00254	98
1320	174·5	0·00248	
1920	166·0	0·000216	
2520	158·0	0·000216	
3120	149·5	0·000225	
3720	143·5	0·000224	
4320	138·5	0·000224	

TABLE III *a*.

0	200·0	—	—
60	195·5	0·000767	102
300	189·0	0·000388	103
600	184·0	0·000290	103
900	179·5	0·000255	104
1320	174·0	0·000228	
1920	166·0	0·000216	
2520	158·0	0·000216	

TABLE IV.

Wire No. 1 heated in vacuum for 2 mins. above 1000°.

P_{CO_2} = 100·0 mm. P_{H_2} = 100·0 mm. Temp. = 1200°.

0	200·0	—	—
60	177·5	0·00424	102
90	173·0	0·00349	103
120	168·0	0·00321	101
180	158·5	0·00297	100
240	151·0	0·00280	
300	144·0	0·00273	
420	132·0	0·00272	
480	127·0	0·00272	
540	122·0	0·00270	

Initial Stages of the Reaction.

In all the experiments on this reaction with platinum wire, it was noticed that there is an initial part where the reaction rate is high to start with ; it rapidly falls and assumes a steady value. This interesting observation was also noticed and confirmed with two other platinum wires from the same source. First, the possibility of minute traces of oxygen in the carbon dioxide giving rise to the initial rapid rate, was put to a rigorous test. Carbon dioxide was carefully prepared and analysed each time. Since in all the experiments pure carbon dioxide was used, the idea of small amounts of oxygen giving rise to this effect is completely disproved.

It is possible that this initial fall is due to the rapid poisoning of the catalyst by the carbon monoxide formed in the reaction itself. Experiments were performed at 915° with wire No. 2 in which 100 mm. of carbon monoxide were added to the usual mixture of 100 mm. of carbon dioxide and 100 mm. of hydrogen. The results of two such experiments are given in Fig. 2. The instantaneous rates are plotted against the mean times.

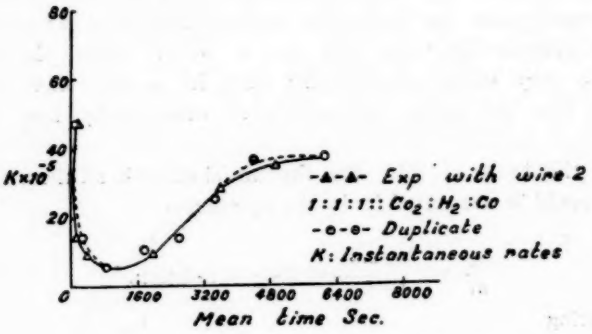


Fig. 2.

With a large excess of carbon monoxide—a reaction product—as diluent, the reaction started with a lower velocity than in its absence, rapidly fell to a minimum and seemed to recover

slowly, though it never reached its original value. With 100 mm. each of carbon dioxide and hydrogen at this temperature, the velocity coefficient at the steady stage is 0·0111 ; but in the presence of 100 mm. of carbon monoxide it started at 0·00049 and fell still lower. It is rather surprising that even if there be carbon monoxide in the system to start with there is still the initial fall in the reaction rate. This seems to suggest that the carbon monoxide formed on the surface in the reaction itself poisons the catalyst.

It is not impossible that of the 'active centres' of the catalyst, some are 'more active' than the rest and hence more susceptible to poisoning. If the adsorbed carbon dioxide and hydrogen, on these 'more active' centres react to form carbon monoxide and water, it is likely that the freshly formed carbon monoxide does not get desorbed from those centres ; thus the 'more active centres' are rapidly poisoned by carbon monoxide leaving only a surface less active. This view does not seem to be unlikely when it is known that the heat of desorption of carbon monoxide from a platinum surface is very great and it requires heating of the wire in vacuum at high temperatures of burning with oxygen to remove the adsorbed carbon monoxide (*cf.* Langmuir, *Trans. Farad. Soc.*, 1922).

The existence of 'more active centres' on the surface appears to be reasonable, for prolonged heating of the wire in vacuum as in the experiments with wire No. 3 (cited later), the initial effect is very nearly eliminated ; since it is the more active centres that are easily susceptible to sintering by heat treatment.

On the basis of this idea the initial effect in all these experiments could be accounted for by the equation—

$$\frac{dx}{dt} = \frac{k(a-x)}{1+cx} = \text{Rate of reaction.}$$

Integrating

$$k = \frac{1+ac}{t} \log \frac{a}{a-x} - cx/t$$

where k = velocity constant,
a = initial pressure of hydrogen,
x = CO formed in time t.
c = a constant.

The same equation has been used by Hinshelwood and Prichard (*J. Chem. Soc.*, 1925, **127**, 327) in their study of the decomposition of nitrous oxide at the surface of platinum where oxygen poisons the catalyst.

In order that this equation may hold good for the initial stages, it is necessary that the graph for $1/t \log a/a-x$ and x/t ought to be a straight line in the initial stages. In all the experiments it is found that this equation gives a straight line for the initial part of the reaction. Some of the graphs are given in Fig. 3, *a*, *b*, *c*, *d*, & *e* (K_0 in the graphs stands for $1/t \log a/a-x$). It is interesting that the first experiment with the wire does not give uniform velocity coefficients ; but the above equation is seen to be applicable for the entire range of the reaction and all the experimental points lie on a straight line (Fig. 3*a*) Table II gives the data for the first reaction with wire No. 1 and Table V that for wire No. 3.

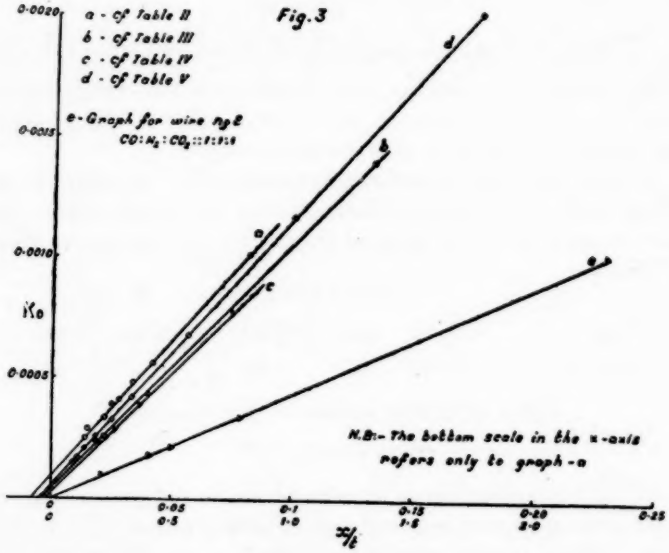


TABLE V.

P_{CO_2}=101·9 mm. Wire No. 3.

P_{H_2}=102·2 mm. Temperature=942°.

Time (sec.).	Total press. (mm.).	R.
0	204·1	—
150	176·5	0·00210
300	173·0	0·00121
600	169·0	0·000701
1200	163·0	0·000427
1800	158·4	0·000338
2700	153·2	0 000262
3900	149·0	0·000204
5400	144·1	0·000168
6300	142·3	0·000152

The last column in the Tables II, III and IV refers to the slope of the equation. It is given by $(1/c+a)$.

$$k/c = (\frac{1}{c}+a).\ \frac{1}{t}\log\ \frac{a}{a-x} - \frac{x}{t}$$

$$= (\frac{1}{c}+a)\ K_0 - \frac{x}{t}$$

where K_0=unimolecular coefficient given by $1/t \log a/(a-x.)$

The values for K_0 and x/t are plotted and the value for x/t when $K_0=0$ gives the value of K/c ; for if $K_0=0$, $K/c=-x/t$, from which by substitution $(1/c+a)$ is calculated.

Even in those experiments with excess of carbon monoxide in the gaseous mixture this equation holds good for the initial stage. For those two experiments the slope of the line for the equation is given in Table VI.

TABLE VI.

Expt. I	235	237	230	220
Expt. II	230	229	228	221

Effect of an Inert Diluent on the Reaction.

(With wire No. 1)

Nitrogen has been tried as an inert diluent in the system. Experiments were conducted with 100 mm. of each of carbon dioxide and hydrogen with varying pressures of nitrogen from 100 to 300 mm. at 1200°. The reaction proceeded as usual with the initial peculiarity. The velocity coefficients in the steady stage were the

same as those in the experiments without nitrogen (*cf.* Tables IV and VII). But when about 70 mm. of carbon monoxide had formed in the system the velocity coefficients slowly fall off. This was noted in all the experiments with nitrogen in those cases where there was no nitrogen in the system the reaction rates were all constants even when 70 mm. of carbon monoxide were formed in the system. (*cf.* Table IV).

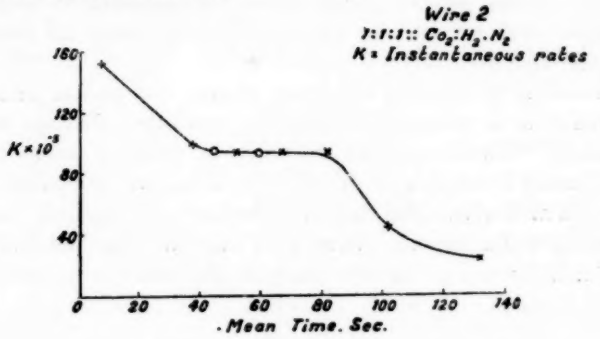


Fig. 4.

A good example is given in Fig. 4, being an experiment at 915° with wire No. 2. The instantaneous rates are plotted against the mean times. The velocity coefficients in the steady portion is 0·0100 while that of the reaction without nitrogen was 0·011 (experiment not quoted).

TABLE VII.

Wire No. 1 heated in vacuum for 2 mins. at 1000°.

$P_{CO_2} = 100{\cdot}6$ mm. $P_{H_2} = 101{\cdot}2$ mm. $P_{N_2} = 101{\cdot}0$ mm. Temp. = 1200°.

(*N. B.*—For experiment without nitrogen see Table IV).

Time.	Total press.		R
0 sec.	302·7mm.	0·0137	
30	268·4	0·00773	
60	265·8	0·00492	
120	257·5		
180	247·6		0·00230*
240	239·8		0·00277
300	235·0		0·00285
360	232·0		0·00268
480**	229·0		0·00248

* Calculated from the steady portion of the reaction.

** After this reading the coefficients fall off.

That nitrogen has no effect on the reaction rate is at variance, with the conclusion arrived at by Constable (*Proc. Camb. Phil. Soc.*, 1926, **23**, 172) from purely theoretical considerations. The time of stay of an adsorbed molecule on the surface is not dependent on the pressure, for in chemical reactions proceeding at a surface, the adsorbed molecule is released only after its activation. If this activated molecule is evaporated it may be replaced by the reactant or the diluent. From these considerations it is to be concluded that nitrogen is not capable of replacing the reactants from the surface.

The fall in the reaction rate when 70 mm. of carbon monoxide are formed in the presence of nitrogen is peculiar. Perhaps at the later stages when the reactants are small in quantity more of the active surface is left free for the adsorption and the poisoning of it by carbon monoxide. But that this effect is to be noticed only in the presence of nitrogen is difficult to explain. The possibility of experimental errors at the later stages of the reaction is not completely shut out.

Temperature coefficient of the reaction velocity.

(With wire No. 3).

It appears rather difficult to obtain any idea of the temperature coefficient of the reaction velocity for the interaction of carbon dioxide and hydrogen on the surface of platinum, for the activity of the wire changes with use and there is a rapid fall in the velocity coefficients in the initial stages. These difficulties were overcome by carrying out a series of reactions at differert temperatures alternately going up and down and heating the wire in vacuum at about 1000° for 5 mins. before each experiment. The behaviour of the wire throughout the operations is interesting and it is enough to mention that such a procedure deactivates the wire. Thus after working 980° and at 1060°, if the reaction was carried out at 980° the activity of the wire was lowered by 50%.

A series of experiments was carried out alternately at higher and lower temperatures with heating of the wire between any two experiments till reproducible values were got. Tables VIII and IX give the results of experiments at 980° and 1060° respectively. The resistance of the wire at 0° after heating in vacuum was found and used in the calculation of these temperatures. It is interesting

to note in passing that heating the wire in vacuum for long periods almost eliminates the initial peculiarity noted with the fresh wire. Perhaps the 'more active centres' are destroyed due to sintering.

TABLE VIII.

Wire heated in vacuum for 5 mins. at about 1000°.

P_{CO_2} = 101·1 mm. P_{H_2} = 102·9 mm. Temp. = 980°.

Time.	Total pressure.	Instantaneous rates.
0 sec.	204·0 mm.	—
30	198·5	(0·00183)
60	195·3	0·00111
90	192·0	0·00119
150	187·0	0·00095
300	176·0	0·00091
600	158·2	0·00090
960	144·1	0·00094
1200	132·6	0·00103
1500	124·4	0·00100
		Mean 0·00100

TABLE IX.

Wire heated in vacuum for 5 mins. at about 1000°.

P_{CO_2} = 102·9 mm. P_{H_2} = 101·1 mm. Temp. = 1060°.

0	204·0 mms	—
30	196·2	0·00267
60	189·3	0·00256
90	183·0	0·06252
120	177·1	0·00255
150	171·4	0·00266
180	166·8	0·00232
240	158·9	0·00236
300	152·1	0·00249
360	145·9	0·00229
		Mean 0·00249

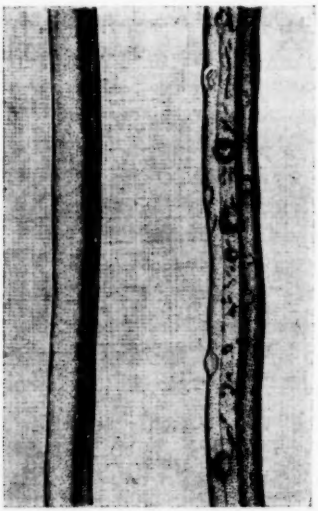
Thus the velocity constant rises by about 2·5 times for a rise in temperature of 80° in the neighbourhood of 1000° giving an apparent heat of activation of 38,000 calories, as calculated from Arrhenius' formula (*cf.* Hinshelwood, *loc. cit.*).

Resistance of the wire.

It is possible that as the wire changes its activity with use, the resistance of the wire might also change. But the resistance of the wire while hot did not show much variation. In the course of an experiment the resistance of the hot wire was 12·71 ohms, while that in the next experiment it was 12·76 ohms. The small change of 0·06 ohms even if taken as reliable, gives only a difference of about 10° in the calculated temperatures, which is within the experimental error and is negligible. But the resistance of the wire at the melting point of ice at various stages of the treatment given to it showed appreciable variation, which has to be taken into account in calculating the temperature.

Wire No. 3.

Resistance of the fresh wire at 0°	=2·7645 ohms.
Resistance of the wire at 0° after two experiments conducted with it at 940°.	=2·7880
Resistance of the wire at 0° after the experiments in Table IX.	=2·8465



After Before

PLATE I.

The Surface of the Wire.

The wire was examined under the microscope before and after the experiments. Since the wire under high magnification could not be focussed well, microphotographs could not be taken. But however, parts of the surface of wire were observed through the microscope and the picture of the surface drawn with the aid of a camera lucida.

The surface of the wire (Plate 1) before the experiments appears granular and rough. After the experiments it appears quite smooth and regular; it shows a sintered appearance.

The heating of the wire in vacuum to drive off the adsorbed carbon monoxide, was seen to deactivate it to a decided extent. It shows that the granular parts of the surface which according to Taylor (*Proc. Roy. Soc.*, 1925, **108A**, 105) contain the active centres of the surface, are sintered and thus leaves comparatively less active surface. Such a view seems most probable espacially when it is known that a more active catalyst is the one which is more susceptible to poisons and also more sensitive to heat treatment. The reaction with a new piece of wire (*cf.* Tables II and V) is highly retarded by carbon monoxide. Subsequent reactions where the more active centres are held up by carbon monoxide or sintered by heat treatment, proceed with the usual unimolecular velocity without being retarded by carbon monoxide except in the initial stages. Heating it in vacuum for long periods eliminates the initial fall, for the active points on the surface are destroyed. Thus it appears that a rough surface is more active than a smooth one.

This conclusion was confirmed in the following way. The platinum wire No. 3 used in the last experiments was scratched a number of times with fine emery flour spread out on a bit of moist filter paper, thus creating rough surface. The resistance of the wire at the melting point of ice was measured after rubbing it with emery. It was 2·8526 ohms. Table X gives the results of a reaction carried out with the rough wire.

TABLE X.

Wire scratched with emery.

$P_{CO^2} = 103{\cdot}5$ mm. $P_{H_2} = 101{\cdot}5$ mm. Temp. = 1040°.

Time.	Total pressure.	Instantaneous rates.
0 sec.	205·0 mm.	—
30	199·3	0·00192*
60	192·5	0·00231
90	185·9	0·00255
120	179·1	0·00287
150	173·0	0·00280
180	167·1	0·00293
210	162·0	0·00278
240	157·0	0·00299
270	151·8	0·00341
300	147·4	0·00318

The temperature of this reaction was calculated with the resistance at 0° found out after scratching the wire with emery. It is noticed that at 1040° (Table X) with the rough wire, the reaction rate is decidedly higher than at 1060° (Table IX) with a smooth wire. Hence the roughness of the surface seems to be a factor of importance in catalysis.

Summary and Conclusions.

1. The interaction between carbon dioxide and hydrogen has been studied at the surface of platinum wire.

2. The fresh wire is poisoned by the carbon monoxide formed on the surface.

3. The reaction is unimolecular except for an initial fall in the reaction velocity which has been shown to be due to the rapid poisoning of the ' more active ' centres of the catalyst surface by the carbon monoxide formed thereon.

* The temperature of the wire was on the low side to start with.

4. Heating in vacuum for a long time at high temperatures almost eliminates the initial fall in the reaction rate. The wire is deactivated to a great extent.

5. The resistance of the wire increases on heating in vacuum for a long time.

6. An inert diluent like nitrogen does not affect the reaction rate.

7. The surface of the wire is changed from a granular to a sintered one after the experiments.

8. A rough surface is more active than a smooth or a sintered one.

9. The energy of activation for this reaction at the surface of platinum wire is 38,000 calories.

In conclusion I wish to express my thanks to Professor H. E. Waston for the kind interest, helpful criticism and very many hints and suggestions as regards practical methods of manipulation.

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Reactions at the Surface of Hot Metallic Filaments. Part II. The Reaction $H_2+CO_2 \rightarrow CO+H_2O$ on Platinum-iridium Alloys.

By B. S. Srikantan.

In Part I the interaction between carbon dioxide and hydrogen on the surface of platinum has been described. The present paper presents the results of the experiments with platinum-iridium alloys used as catalysts. Alloys containing 5, 10, 15, 20, 25 and 30 per cent. of iridium have been used. The object of the investigation was to study if the composition of the alloy or the nature of the surface is responsible for the activity. Incidentally it was thought that these experiments would throw some light on the nature of promoters or mixed catalysts.

Experimental.

The apparatus and the experimental methods were the same as in the first part, except that a different method was adopted for the measurement of the temperature of the wire. The alloys are known to have a very low temperature coefficient of resistance and hence the calculation of the temperature from the data on resistance would be inaccurate. The temperature was measured with the aid of an optical pyrometer, specially constructed for the purpose.

The pyrometer was first calibrated with reference to pure platinum wire (whose temperature was known from its temperature coefficient of resistance), at various temperatures, against an accurate voltmeter across the pyrometer lamp. The glow of these wires, when in use, was matched with the filament of the pyrometer and the voltmeter readings taken. With the help of the volt-temperature graph, the temperature of the wire was obtained.

It must however be pointed out that this method of measuring temperature is not free from defects. There is a great deal of personal error in matching the intensity. Great difficulty was experienced due to slight differences in colour of the two glowing filaments, though their brightness was equal. To overcome this difficulty a piece of red glass was interposed on the observation side.

Moreover, the wire has to be observed through a layer of about 2 cms. of water (*cf.* Part I) the glass walls of the Dewar flask and the reaction vessel. Further there is always a thin film of moisture on the outer side of the Dewar vessel, for the water inside is at 0° and this thin film of moisture is persistent and could not be wiped off completely. All these factors contribute to give a lower value for the temperature than it actually is (*cf.* Retzow, *Z. Vereins. Deutsch. Ing.*, 1923, **67**, 179). However care was taken to maintain the conditions similar in all the experiments involving the use of the optical pyrometer, which was itself calibrated under similar conditions. The Dewar vessel was surrounded on all sides except the observation side by means of a black paper in order to avoid all optical illusions arising out of the varying brightness of the room during the various seasons. The values are comparable among themselves. Within a fair degree of accuracy it is possible to say that the actual temperatures recorded might be about 2 per cent. in error in the neighbourhood of 1000°.

All the wires used in these experiments were as before 24 cm. long and 0·01 cm. in diameter.

The Results.

Platinum-iridium alloy containing 5 per cent. of iridium.—The wire was quite steady in activity and the data could be duplicated. The following tables give the results at various temperatures.

TABLE I.

P_{CO_2} = 104·3 mm. P_{H_2} = 100·4 mm. Temperature = 870°.

Time (sec.) ...	—	0	15	30	45	60	75	90
Total press (mm.)	204·7	200·6	183·3	169·0	157·4	148·0	140·1	133·9
Unimolecular constants ...	—	—	0·0133	0·0132	0·0132	0·0132	0·0132	0·0131
							Mean	0·0132

TABLE II.

P_{CO_2} = 105·1 mm. P_{H_2} = 107·8 mm. Temperature = 915°.

Time (sec.)	—	0	10	20	30	40
Total press (mm.) ...	212·9	198·9	176·5	161·8	149·4	140·9
Unimolecular constants ...	—	—	0·0272	0·0252	0·0250	0·0242
					Mean	0·0254

Note:—The reaction is so rapid that it is not possible to raise the wire to the required temperature all at once. So a few seconds were taken to adjust the current till a balance was got in the bridge and hence the time is not noted in the above two tables at the beginning. The constants are calculated after the reading marked with an asterisk. It is just possible that this would interfere in the observation of any peculiarity in the initial stages of the reaction as in the case of platinum wire. But a careful experiment in Table III shows that with this wire there is no peculiarity in the initial stages.

TABLE III.

P_{CO_2} = 102·5 mm. P_{H_2} = 112·8 mm. Temperature = 930°.

Time (sec.) ...	0	10	20	30	40	50
Total press. (mm.) ...	215·3	187·4	166·8	152·0	141·5	133·5
Unimolecular constants ...	—	0·0284	0·0281	0·0276	0·0267	0·0258
					Mean	0·0273

The reaction in the above experiment was allowed to proceed till about 84 per cent. and the gas analysed.

TABLE IV.

Percentage of gases.	CO_2	CO	H_2	CH_4
By calculation. ...	2·83	85·28	11·79	—
By analysis. ...	3·17	85·05	11·78	—

Hence in this reaction there seems to be no possibility of any other side reaction involving the production of methane.

The temperature over which the reaction could be studied is very limited. Below 850° the optical pyrometer is not very reliable and above 950° the reaction is too fast to be kept under control. The energy of activation calculated from the above data is 36,000 cals.

A microscopic study of the surface of wires before and after the reaction does not show prominent changes in the surface (*cf.* Plate I)

Platinum-iridium alloy containing 10 *per cent. of iridium.*—Unfortunately a systematic investigation of this wire could not be made, as the wire snapped due to an explosion caused by the introduction of oxygen into the gas mixture by mistake. The surface of the wire after this explosion presented a sintered appearance (*cf.* Plate II) and small beads had collected on the surface. The broken wire was spot welded by means of a tiny arc and a few experiments were carried out. Figure 1 gives the summary of the results obtained with this

wire at 935°. It is evident that the activity of the sintered catalyst is far lower than that of the fresh one. Perhaps the active centres which are responsible for strong adsorption of the reacting gases were destroyed due to the heating in the explosive mixture.

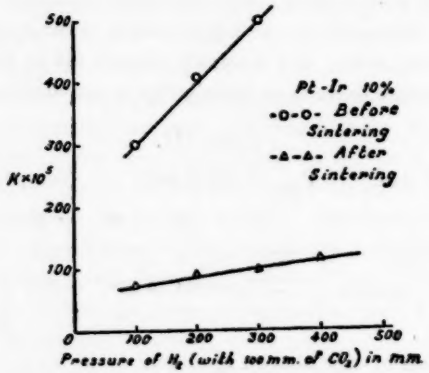


Fig. 1.

Platinum-iridium alloy with 15 *per cent. of iridium.*—The wire was steady in activity and the results were reproducible. The following tables give the velocity constants at various temperatures. A microscopic study of the surface before and after the experiments did not show any great change. It is similar to the 5 per cent. alloy (*cf.* Plate I).

TABLE V.

P_{CO_2} = 99·8 mm. P_{H_2} = 109·9 mm. Temperature = 895°.

Time (sec.) ...	0	150*	750	1050	1350	1650	1950
Total press (mm.)...	209·7	204·7	158·4	142·0	130·0	122·4	111·5
Unimolecular constants ...	—	—	0·00097	0·00101	0·00104	0·00097	0·00100
						Mean	0·00100

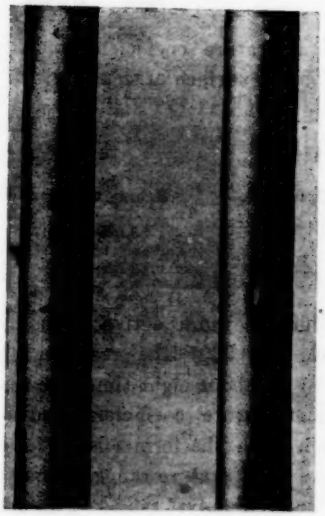
* Error in adjusting the temperature at first.

TABLE VI.

P_{CO_2} = 99·7 mm. P_{H_2} = 103·5 mm. Temperature = 935°.

Time (sec.) ...	0	30*	60	90	120	150	180
Total press (mm.)...	203·2	190·5	182·0	174·1	167·0	160·5	155·0
Unimolecular constants ...	—	—	0·00327	0·00331	0·00331	0·00331	0·00331
						Mean	0·00331

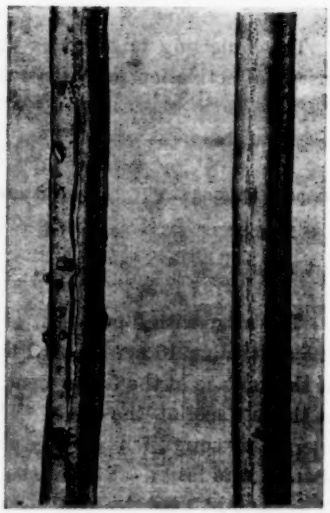
Pt-Ir wire (5%)



Befere After

PLATE I.

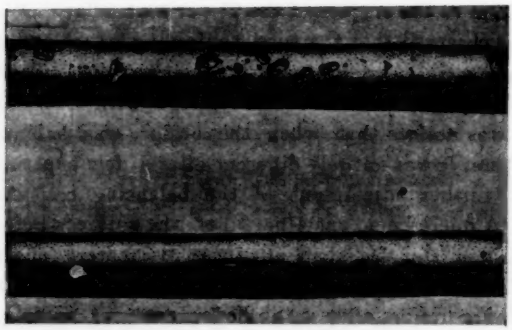
(Pt-Ir wire (10%)



After Before

PLATE II.

Pt Ir wire (20%)



After

Before

PLATE III.

* Temperature on the high side at first.

TABLE VII.

P_{CO_2} = 101·1 mm. P_{H_2} = 109·7 mm. Temperature = 975°.

Time (sec.) ...	...	0	15	45	75	105	135
Total press (mm.)	...	210·8	201·5	184·8	171·5	161·0	151·9
Unimolecular constants.	...	—	0·00591	0·00600	0·00591	0·00580	0·00580
						Mean	0·00588

The following table gives the temperature coefficient and the energy of activation for the reaction on the surface of this wire.

TABLE VIII.

Temperature range.	Temperature coeff. for 10°.	Energy of activation.
895°—935°	1·35	83,000 cals.
935°—975°	1·15	43,000 ,,

The alloy with 5 per cent. of iridium is more active than the one containing 16 per cent. of iridium. At 930° the reaction rate at the surface of the 5 per cent. alloy is about eight times as that at the surface of the other. The temperature coefficient and the energy of activation for the reaction with the former is far lower than that of latter at about the same temperature range. This is in agreement with the idea that an active catalyst renders available the energy of activation at a far lower temperature than a comparatively poor catalyst. So it is not surprising that an increase in temperature lowers the temperature coefficient and the energy of activation at the surface of the 15 per cent. alloy.

It was observed that the wires containing 20, 25 and 30 per cent. of iridium were very unsteady in their activity. Their resistance and probably their surface also change with use. In all these cases it was noticed that when the bridge was balanced for one temperature, it was entirely different after a few experiments without any further adjustment of the balancing resistances of the bridge. A microscopic examination of the surfaces before and after the experiments shows that all these wires were affected more or less in the same way. Plate III gives an example.

Platinum-iridium alloy with 20 per cent. of iridium.—To start with, the wire was not steady in activity. The velocity coefficients

were not constant. But after a few experiments unimolecular velocity constants were obtained, though their values varied from experiment to experiment. In four experiments carried out in succession the velocity constants at 945° with 100 mm. of each of carbon dioxide and hydrogen were 0·00694, 0·00390, 0·00141, 0·00055 respectively. Perhaps this behaviour is due to the poisoning of the surface by carbon monoxide. So the wire was heated in vacuum for one minute at about 1000°. It was found that the resistance of the wire changed such that the temperature of the wire measured by the pyrometer was slightly higher than the previous value, without any change in the bridge coils. The velocity constant increased to 0·00089. Further heating in vacuum for a minute before the next experiment did not make any change in the temperature of the filament but the velocity constant of the reaction was slightly higher than the previous one. The following table gives a summary of the results of experiments carried out with 100 mm. of each of carbon dioxide and hydrogen at 960° aad the wire being heated in vacuum for one minute at about 1000° before each experiment.

TABLE IX.

Experiment No.	75	76	77	78
Unimolecular velocity constant. (mean value)	0·00089	0·00109	0·00207	0·00269

TABLE X.

Experiment No.	79	80	83	85
Unimolecular velocity constants. (mean value)	0·00278	0·00337	0·00360	0·01050

The progressive increase in the activity of the wire is perhaps due to the liberation of the adsorbed carbon monoxide every time the wire is heated in vacuum. Table X gives the results of a series of experiments carried out at 960° after heating the wire in vacuum for 5 minutes at about 1000° before each experiment.

The following table shows that if the wire was heated for a longer period (10 minutes) the activity is so increased that even at 865° the reaction is too fast to be measured.

TABLE XI.

[Heated the wire in vacuum for 10 mins.]

P_{CO_2} = 102·5 mm. P_{H_2} = 103·3 mm. Temperature = 865°.

Time (sec.)	0	15*	30	45	60
Total press. (mm.) ...	205·8	187·4	154·0	137·9	129·5
Press. of H_2 (mm.) ...	103·3	84·9	51·5	35·4	27·0

Since it is very difficult to drive off the adsorbed carbon monoxide from the surface it was thought better to burn it off. So a small quantity of oxygen was introduced in the reaction mixture and the wire was burnt in it. But it was found that such a procedure lowered the activity of the wire to a great extent. While the reaction went to 70 per cent. in 60 seconds at 865°, after burning it in oxygen, the reaction went to only 50 per pent. in 360 seconds.

The results of gas analysis quoted in Table XII show that the reaction products are only carbon monoxide and water and that no other side-reaction is possible.

TABLE XII.

Experiment No.	Percentage composition.	CO_2	CO	H_2	CH_4
82	By calculation	22·52	53·33	24·15	—
	By analysis	22·05	55·37	22·87	Nil
90	By calculation	34·07	32·40	33·57	—
	By analysis	33·72	33·14	33·14	Nil

Platinum-iridium alloy with 25 per cent. of iridium.—This wire is also interesting in that its resistance changes with use, so that its temperature when first adjusted at 965°, fell to 925° without further adjustment ; and again rose to 1105° by itself. But this wire gave for the velocity coefficients steady values. The resistance did not change in the middle of an experiment.

Table XIII gives a summary of few experiments carried out with this wire with 100 mm. of each of carbon dioxide and hydrogen.

TABLE XIII.

Experiment No. ...	101	102	103	104	105	106	107	108
Temperature ...	965°	925°	985°	1025°	1050°	1065°	1075°	1100°
Unimolecular constants (mean value).	0·00188	0·00105	0·00202	0·00388	0·00550	0·00679	0·00748	0·00800

* The temperature was slightly on the lower side to start with.

In these experiments the possibility of the drift in the activity of the wire corresponding to changes in resistance has to be recognised. Hence the above data cannot be used to calculate the temperature coefficient of the reaction.

Platinum-iridium alloy with 30 per cent. of iridium.—This wire was found to be very active and in general behaved in the same way as the previous wire. The following table gives the data for the reaction at 1000°. Even when the temperature was lowered to 920° in the subsequent experiments the reaction rate did not fall down. In fact it was 25 per cent. faster than at 1000°. The reaction went to about 80 per cent. in a minute and a quarter. So further work with this wire was abandoned.

TABLE XIV.

P_{CO_2} = 101·7 mm. P_{H_2} = 101·6 mm. Temperature = 1000°.

Time (sec.)	0	30*	45	60	75	90	105
Total press. (mm.)	203·3	169·5	149·1	133·3	123·3	117·5	113·6
Unimolecular constants	—	—	0·0204	0·0226	0·0220	0·0228	0·0221
						Mean	0·0221

Summary and Conclusions.

1. The interaction between carbon dioxide and hydrogen has been studied at the surface of platinum-iridium alloys containing 5, 10, 15, 20, 25 and 30 per cent. of iridium.

2. The 5 per cent. alloy is more active than either the 10 or 15 per cent. alloy. The 30 per cent. alloy is the most active of all the catalysts and the reaction rate could not be controlled with any degree of accuracy for even at 920° the reaction went to 80 per cent. in a minute and a quarter. The activity does not seem to have any correlation with the composition of the alloys.

3. The temperature coefficient and the heats of activation have been calculated for the reaction with 5 and 15 per cent. alloys. The energy of activation with a powerful catalyst is lower than that with a poor catalyst at about the same temperature range.

* Temperature on the low side to start with.

4. It was observed that in the case of the 10 per cent. alloy the sintered surface is less active than an unsintered one.

5. The alloys containing 20, 25 and 30 per cent. of iridium change their activity with use. This is partly due to the strong and irreversible adsorption of carbon monoxide and partly due to the changes in the nature of the surface. In the case of the 20 per cent. alloy heating in vacuum improves the activity perhaps due to the explusion of carbon monoxide from the surface.

6. The resistance of the wires (20, 25 and 30 per cent. alloys) changes slowly from experiment to experiment.

The surfaces of these wires have been examined microscopically before and after the experiments. The alloys with 20, 25 and 30 per cent. of iridium show more or less similar changes.

In conclusion I wish to express my best thanks to Prof. H. E. Watson for his kind interest and helpful criticism.

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Reactions at the Surface of Hot Metallic Filaments. Part III. The Reaction $CO_2 + H_2 \rightarrow H_2O + CO$ on Platinum coated with Barium Oxide.

By B. S. Srikantan.

The interaction of carbon dioxide and hydrogen at the surface of platinum is unimolecular. The order of the reaction being unity at the surface of a catalyst could be explained in a satisfactory manner by exactly the same assumptions as were made by Hinshelwood ("Kinetics of Chemical Change in Gaseous Systems," 1926, p. 148). If one of the reacting gases is adsorbed in preference to the other, the reaction rate is solely governed by the rate at which the molecules of the other gas strike those of the adsorbed one, provided every such collision is effective. In the reaction between carbon dioxide and hydrogen at the surface of platinum and platinum-iridium alloys, described in the previous parts, it is difficult to judge if carbon dioxide or hydrogen, which is being preferentially adsorbed. But if the surface is coated with a thin layer of oxide it is possible that the oxide surface would be favourable for the adsorption of carbon dioxide to a greater extent than that of hydrogen and might lead to interesting results. With this object in view the reaction has been studied in detail at the surface of platinum wire coated with barium oxide.

The platinum wire (No.3), used for the experiments in Part I, was coated with a thin layer of barium oxide. The usual method of coating the wires with the help of paraffin sticks containing the oxide was not adopted, since it did not lead to satisfactory results. The coating pealed off and there was a tendency for the oxide to collect in small lumps at several places along the wire. So the wire was dipped in a concentrated solution of barium nitrate for a few minutes. Then it was slowly warmed up by sending a small current through it, just to drive off the water. This was repeated several times till a thin uniform layer of barium nitrate was formed on it.

Next the wire was electrically heated to bright redness in vacuum to decompose the nitrate and a little of the carbonate formed on it, and the apparatus was exhausted while heating the wire. Thus a uniform and thin layer of barium oxide was deposited on the surface.

The experimental methods were the same as in Part I. The temperature was calculated from the resistance of the wire on the assumption that the layer of oxide is a non-conductor.

At the temperature at which these reactions have been carried out, it should be remembered that most of the oxide would be converted into the carbonate and the surface would be composed of a mixture of barium oxide and barium carbonate. It is not impossible that the surface might be all of barium carbonate with a few specks of barium oxide, for the dissociation pressure of the former is 750 mm. at 1350°, 2·7 mm. at 1000° and 0·4 mm. at 915° (Frankelstein, *Ber.*, 1906, **39**, 1585; Johnston, *J. Amer. Chem. Soc.*, 1908, **30**, 1356). Hence the active catalyst in this instance is a few points on the surface, chiefly composed of the complex BaO, $BaCO_3$.

This catalyst was steady in activity and the results could be reproduced by working even at higher and lower temperatures alternately.

The Influence of Temperature.—The following tables give the data for the reaction velocity at different temperatures.

TABLE I.

P_{CO_2} = 100·6 mm. P_{H_2} = 105·4 mm. Temperature = 826°.

Time (secs.).	Pressure of hydrogen.	Instantaneous rates.
0	105·4 mm.	—
22	84·6	0·0100
52	62·5	0·0100
82	44·9	0·0109
112	33·2	0·0099
142	25·0	0·0093
	Mean	0·0100

TABLE II.

P_{CO_2} = 100·1 mm. P_{H_2} = 102·1 mm. Temperature = 612°.

Time (secs.).	Pressure of hydrogen.	Instantaneous rates.
0	102·1 mm.	—
30*	99·9	—
270	88·9	0·000485
570	77·6	0·000452
870	66·9	0·000493
1170	57·9	0·000481
	Mean	0·000478

* The temperature was on the high side to start with and the time interval is short; so this reading is left out of consideration.

N. B.—The instantaneous rates are given by $dp/dt \times 1/P_{Hm}$ where dp is the change in pressure in time dt and P_{Hm} is the mean pressure of hydrogen in that interval.

TABLE III.

P_{CO_2} = 101·8 mm. P_{H_2} = 102·1 mm. Temperature = 769°.

Time (secs.).	Pressure of hydrogen.	Instantaneous rates.
0	102·1 mm.	—
30*	89·2	—
60	73·6	0·00639
90	60·1	0·00673
120	49·2	0·00665
150	40·2	0·00671
180	33·5	0·00606
	Mean	0·00651

* The temperature to start with was on the low side and hence this reading is left out of consideration.

Table IV gives the values of the temperature coefficients and the energy of activation E, calculated by Arrhenius's formula. The energy of activation and the temperature coefficient fall off with rise of temperature.

TABLE IV.

Temperature range.	Temp.-coeff. for 10°.	E.
612—769°	1·18	27,000 calories.
769—826°	1·08	15,000

The Influence of Pressure of Carbon Dioxide on the Reaction.—Experiments were carried out with 100 mm. of hydrogen and varying amounts of carbon dioxide in the system. The results are described in the following tables.

TABLE V.

P_{CO_2} = 51·2 mm. P_{H_2} = 101·6 mm. Temperature = 769°.

Time (secs.).	Pressure of hydrogen.	Instantaneous rates.
0	101·6 mm.	—
27	89·8	0·00457
57	77·8	0·00477
87	68·3	0·00433
		Mean 0·00456

Table III gives the data for 100 mm. of each of the gases.

TABLE VI.

P_{CO_2} = 202·0 mm. P_{H_2} = 104·8 mm. Temperature = 769°.

Time (secs.).	Pressure of hydrogen.	Instantaneous rates.
0	104·8 mm.	—
30	95·4	0·00313
60	86·0	0·00345
90	75·1	0·00451
120	64·2	0·00522
150	54·0	0·00575
180	45·0	0·00604
210	36·5	0·00695
240	30·0	0·00652
270	24·1	0·00727
330	16·0	0·00673
		0·00670 (mean of last five).

TABLE VII.

P_{CO_2} = 309·7 mm. P_{H_2} = 102·3 mm. Temperature = 769°.

Time (secs.).	Pressure of hydrogen.	Instantaneous rates.
0	102·3 mm.	—
30	81·1	0·00771
60	59·2	0·01040
90	40·3	0·0127
120	27·6	0·0125
160	18·8	0·0126
180	12·3	0·0139
		0·0129 (mean of last four).

TABLE VIII.

P_{CO_2} = 411·8 mm. P_{H_2} = 105·2 mm. Temperature = 769°.

Time (secs.).	Pressure of hydrogen	Instantaneous rates.
0	105·2mm.	
30	83·7	0·00758
60	61·4	0·0103
90	42·0	0·0125
120	28·8	0·0129
150	18·7	0·0136
		0·0127 (Mean of last three).

The results are represented in Fig. 1. It is rather peculiar that the reaction velocity is not constant from the begining, but

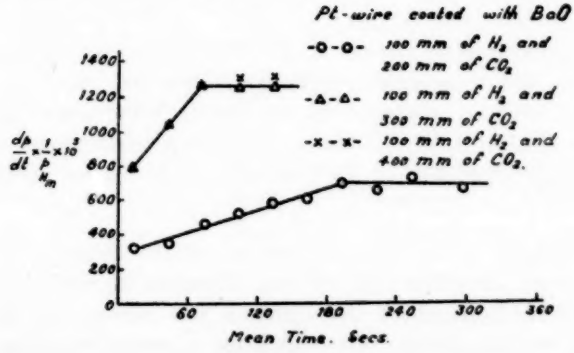

Fig. 1.

slowly rises and then assumes a steady state. This initial rise is noticed in the experiments with 200, 300 and 400 mm. of carbon dioxide in the system. When there was only 100 mm. of carbon dioxide in the system, such a behaviour is not noticed. The results are rather difficult to explain on a quantitative basis. However, these results are enough to give us an idea of the relative adsorptive powers of the surface for these gases. The reaction velocity calculated with reference to carbon dioxide did not come out regular; but that calculated with reference to hydrogen gives fairly good constants except for the initial stages. In Fig. 2 these constants, obtained at the later stages, are plotted aginst varying quantities of carbon dioxide taken.

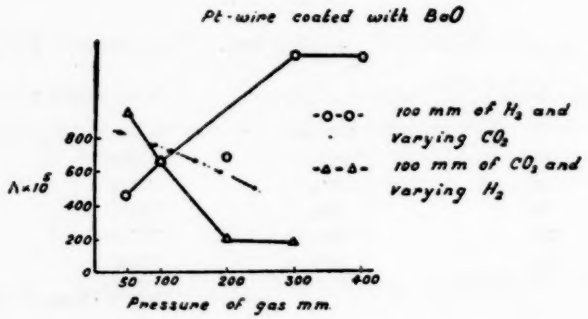

Fig. 2.

The increase of carbon dioxide in the system increases the reaction rate to a great extent till about 300 mm. of carbon dioxide, when it apppears not to change with further increase. Carbon dioxide influences the reaction to a great extent, perhaps due to the tendency of BaO to add on to carbon dioxide and form $BaCO_3$.

Influence of Pressure of Hydrogen on the Reaction.—Experiments were performed with 100 mm. of carbon dioxide and varying amounts of hydrogen in the system. The results are described in the following tables. They show in a general way that hydrogen has a depressing effect on the reaction.

TABLE IX.

P_{CO_2} = 103·0 mm. P_{H_2} = 56·5 mm. Temperature = 769°.

Time (secs.)	Pressure of hydrogen.	Instantaneous rates.
0	56·5mm.	—
30	49·8	0·00424
60	41·9	0·00574
90	32·1	0·00819
120	24·1	0·00949
150	18·0	0·00966
180	13·1	0·01040
210	9·9	0·00928
		0·00940 (mean of last five).

Table III gives the data for 100 mm. of each of these gases.

TABLE X.

P_{CO_2} = 104·3 mm. P_{H_2} = 209·5 mm. Temperature = 769°.

Time (secs.)	Pressure of hydrogen.	Instantaneous rates.
0	209·5 mm.	—
30	206·9	0·000416
120	194·5	0·000686
180	184·5	0·000879
240	174·7	0·000926
300	164·3	0·001020
360	155·1	0·000960
420	146·7	0·000928
480	139·2	0·000880
540	132·7	0·000800
		0·000888 (mean of last seven).

TABLE XI.

P_{CO_2} = 100·0 mm. P_{H_2} = 307·1 mm. Temperature = 769°.

Time (secs.)	Pressure of hydrogen.	Instantaneous rates.
0	307·1 mm.	—
60	287·1	0·00113
120	273·0	0·000815
180	260·5	0·000790
240	249·5	0·000720
300	237·4	0·000830
		0·000789 (mean of last three).

Here again the velocity coefficients do not come out constant from the beginning. There is an intitial rise. The results are represented in Fig. 2. The velocity constants fall down to a low value with increse of hydrogen and then at about 200 mm. of hydrogen, the graph turns sharp and almost runs parrallel to the *X*-axis, showing that further increase in hydrogen does not much affect the rate.

The above results were used to fit in equations of various types ordinarily found applicable for unimolecular and bimolecular reactions. The above method of representation was found to be best. However the results justify the conclusion that carbon dioxide is greatly adsorbed at the surface of the coated wire. The initial peculiarity could not be explained on a satisfactory basis. The activity of the wire was steady and the results could be reproduced.

Summary and Conclusions.

1. The interaction between carbon dioxide and hydrogen has been studied at the surface of platinum wire coated with barium oxide. It is shown that the active catalyst in these experiments is a complex $BaCO_3$, BaO. The reaction is unimolecular.

2. The temperature coefficient and the energy of activation fall off with rise of temperature.

3. Carbon dioxide is greatly adsorbed by the surface and the reaction rate increases with increase of carbon dioxide till 300 mm.

4. Excess of hydrogen has a depressing effect on the reaction.

5. With excess of either gas, constant velocity coefficients are obtained only after the reaction has proceeded some way, the initial peculiarity is too complicated to explain on any satisfactory basis.

I wish to place on record my thanks to Prof. H. E. Watson for his kind interest and helpful criticism.

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Studies in Geometrical Inversion. Part I. Resonance Reactions.

By Panchanan Neogi and Sunil Kumar Mitra.

P. Neogi, Chatterji and S. Neogi (*J. Indian Chem. Soc.*, 1928, **5**, 279) have shown that neither manganese dioxide nor sulphur dioxide alone produces inversion in maleic acid but by the united action of the two, inversion takes place very rapidly, the yield of fumaric acid being much greater than that obtained by Skraup using a mixture of sulphuretted hydrogen and sulphur dioxide solution.

In this paper their work has been confirmed with reference to maleic acid and extended to citraconic and other acids and esters of some geometrical isomers. Further, the reaction has been studied in all its bearing specially with reference to the effect of the products of the reaction on inversion, and the conclusion has become irresistible that the inversion actually takes place in the midst of the chemical reaction between sulphur dioxide and manganese dioxide and that a chemical reaction itself can act catalytically just as a catalytic substance would do. Such reactions as would take place *in the midst of* another chemical reaction have been called "resonance reactions."

Experimental.

Effect of the Action of Sulphur Dioxide and Manganese Dioxide on Geometrical Inversion.

Conversion of Maleic to Fumaric acid.—To maleic acid (1·7 g. in 5 c.c. of water) precipitated manganese dioxide (3-4 g.) was added. On passing sulphur dioxide through the above solution, the latter became clear, and the temperature rose to 70°. Within 3–4 minutes, a white precipitate rapidly separated. This was collected and extracted with absolute alcohol. The residue after removal of alcohol was dissolved in ether, from which colourless crystals of fumaric acid were obtained which sublimed at 200° (yield, 51 per cent.).

With a view to test whether the products of the reaction of sulphur dioxide on manganese dioxide suspended in water produce any inversion, sulphur dioxide was passed through precipitated manganese dioxide (4-5 g.) suspended in 25 c.c. of water until a clear solution was obtained. A solution of maleic acid in warm water was quickly added to the above clear liquid and the temperature was maintained at 60°-70° on a water-bath. Even after considerable time no separation of fumaric acid took place. The experiment was also repeated at 30° as well as at 100° with no better results. The mixed solution which smelt strongly of sulphur dioxide was kept overnight but no fumaric acid separated. This conclusively shows that the resultant products of the reaction of sulphur dioxide and manganese dioxide are in no way responsible for the conversion of maleic to fumaric acid.

Another variant tried was to suspend precipitated manganese dioxide in maleic acid solution and heat to 70°. On passing sulphur dioxide through the filtered solution, no fumaric acid separated even on cooling.

When ferric hydroxide was substituted in the place of precipitated manganese dioxide no inversion took place.

The individual products of the reaction between sulphur dioxide and manganese dioxide in water are manganese dithionate and manganese sulphate. A little sulphuric acid might also be formed by the oxidation of sulphurous acid. With a view to test whether any of these substances (manganese dithionate, dithionic acid, manganous sulphate and dilute sulphuric acid) has any influence on the inversion, the following experiments were performed, when it was found that these substances individually have no influence on the change.

Action of Manganous Sulphate.—A solution of 5 g. of manganous sulphate was added to a solution of 1·7 g. of maleic acid dissolved in 10 c.c. of water. The temperature of the mixture was maintained at 70° in a water-bath even for an hour but no fumaric acid separated on cooling, or when the solution was kept overnight. This proves that manganous sulphate itslef has no influence on the inversion of maleic to fumaric acid.

Manganous Sulphate and Sulphur Dioxide.—A mixture of maleic acid and manganous sulphate solutions (saturated with sulphur dioxide) was heated at 70° for some time but no inversion occurred.

As a solution of sulphur dioxide is partially converted into sulphuric acid when boiled for some time, we thought that the presence of manganous sulphate which is a good oxidising catalyst might facilitate the oxidation of sulphurous to sulphuric acid and the latter might produce inversion, but the negative result obtained here with manganous sulphate and sulphur dioxide shows conclusively that the dilute sulphuric acid solution which might have been formed, has no influence on the inversion. In fact Skraup (*Monatsh.*, **11**, 323) has shown that strong sulphuric acid produces inversion to some extent but the dilute acid does not and often retards it.

Manganese Dithionate.—A clear solution of manganese dithionate was added to a strong solution of maleic acid. No fumaric acid separated on warming for half an hour on the water-bath or when kept overnight.

Dithionic Acid.—A solution of dithionic acid (prepared by the careful addition of dilute sulphuric acid to a concentrated solution of barium dithionate and subsequent filtration) was added to a strong solution of maleic acid and shaken well. No fumaric acid was obtained even when kept overnight.

Action of Water and Sulphur Trioxide.—With a view to test if the formation of sulphuric acid by the action of water on sulphur trioxide is accompanied with inversion, sulphur trioxide crystals were added to a solution of 2·2 g. of maleic acid in 20 c.c. of water. A large amount of heat and fumes were evolved, but no fumaric acid separated, even after being kept at 70° for some time in a water-bath. P. Neogi, Chatterji and S. Neogi (*loc. cit.*) have already shown that such a highly exothermic reaction as the action of water on phosphorus pentoxide does not produce inversion. It would thus be seen that all exothermic reactions do not produce inversion.

Inversion of Methyl Maleate.—In the case of substances insoluble in water aqueous alcoholic solutions are taken. Methyl maleate (3·51 g.) was dissolved in 25 c.c. of absolute alcohol and 25 c.c. of water were added to it, followed by precipitated manganese dioxide (5 g.). A current of sulphur dioxide was passed through it till a clear solution was obtained. The excess of alcohol was evaporated away, when silky shining crystals were obtained. These were collected and crystallised from ether when methyl fumarate, m.p. 101°-102° was obtained (yield, 30-32%).

Inversion of Ethyl Maleate.—Ethyl maleate (4·2 g.) was treated similarly with manganese dioxide and sulphur dioxide. The oily

residue was extracted with ether. The ethereal solution after evaporation and drying was fractionally distilled when ethyl fumarate came over at 216°-218°.

Inversion of Citraconic Acid.—Citraconic acid (2·8 g.) was dissolved in 10 c.c. of water and precipitated manganese dioxide (4-5 g.) was added to it. A current of sulphur dioxide was passed through the solution, until it became clear; the temperature rose to about 65°-70°. The solution after filtration was concentrated in a vacuum desiccator over sulphuric acid. After 2-3 days, crystals separated. These were filtered and dissolved in ether. The ethereal solution when allowed to evaporate, gave sparingly soluble crystals of mesaconic acid, m.p. 202° (yield, 20%). That the substance was mesaconic acid was conclusively proved by its action with ferric chloride, when a reddish solution was obtained which on warming and then allowing to cool, turned to a brown jelly-like substance. When the inversion was effected at 100°, the yield increased to 25%. It would thus appear that the inversion of citraconic to mesaconic acid is effected with greater difficulty than that of maleic to fumaric acid. The products of the reaction of sulphur dioxide and manganese dioxide failed to produce inversion in citraconic acid or esters of maleic acid.

It is further to be noted that in all cases the inversion is only partial, the percentage varying in different cases.

Action of Sulphur Dioxide and Manganese Dioxide on Erucic Acid and Oleic Acid.—Attempts were then made to apply this method to the inversion of more complex substances such as erucic and oleic acids. In all these cases however the results were negative.

Resonance Reactions.

It has conclusively been shown in the foregoing pages that maleic acid and its esters as well as citraconic acid undergo inversion in the midst of the reaction between sulphurous acid and manganese dioxide and that the products of the latter reaction, either singly or jointly, have no effect on the transformation. We have therefore no hesitation in affirming that a chemical reaction can act as a catalyst in effecting chemical transformations. Skraup's experiment with the transformation of maleic acid in the presence of the combined action of sulphuretted hydrogen and sulphur dioxide hitherto remained an isolated one, but the addition of the present results

makes the supposition of a new kind of chemical reaction almost irresistible. It is to be noted that such reactions would be entirely different from what are called " induced reactions." In the latter there is a primary and a secondary reaction and an 'acceptor,' 'actor' and an 'inductor.' In the new reaction, both the reactions are primary and independent of each other and there are no acceptor, actor or inductor, and in fact no reagent common to the two reactions. The chemical reactions that take place in the transformation of maleic to fumaric acid in the presence of manganese dioxide and sulphur dioxide are the following:—

$$2MnO_2 + 3H_2SO_3 = MnS_2O_6 + MnSO_4 + 3H_2O$$

$$\begin{array}{l} H\cdot C\cdot CO_2H \\ \| \\ H\cdot C\cdot CO_2H \end{array} \rightarrow \leftarrow \begin{array}{l} CO_2H\cdot C\cdot H \\ \| \\ H\cdot C\cdot CO_2H \end{array}$$

It will readily be seen that the two reactions are entirely different from the primary and secondary reactions of an " induced reaction."

We have taken the word ' resonance' from a paragraph in Skraup's writing and named this new kind of chemical reaction 'resonance reaction' which might be defined as a chemical reaction which takes place in the midst of another chemical reaction but not in the presence of any of the reactants singly nor in the presence of the products of the latter reaction.

Geometrical inversions have, up to this time, been the only instances of resonance reactions. Other kinds of reactions are being experimented upon.

Whether an exothermic reaction sets up vibrations or not as postulated by Skraup in effecting geometrical inversion, is in the words of Cohen " beyond reach of experimental proof or disproof " and is not relied on here. We simply maintain that the energy liberated by specific exothermic reactions causes geometrical inversion by activation of the labile isomer. This is the explanation we are at present offering to explain the effect of " resonance reaction". Further work on the subject is proceeding.

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On the Photochemical Oxidation of Formaldehyde by Hydrogen Peroxide in Acid Medium with Tungstic Acid Sol as Photo-catalyst.

By J. C. Ghosh and Sunil Kumar Nandy.

In a previous communication from this laboratory, Ghosh and Mukherjee (*J. Indian Chem. Soc.*, 1929, **6**, 231) have studied the photochemical oxidation of glucose by hydrogen peroxide in acid medium, with tungstic acid sol as photo-catalyst. The results obtained were in many respects somewhat peculiar and it was thought desirable to study in greater detail the photochemical oxidation of formaldehyde in presence of tungstic acid sol.

It may be stated at the outset that the general features of the photo-oxidation of formaldehyde are very similar to that of glucose. As in the case of glucose, here also the conditions of experiment were so arranged that tungstic acid sol behaved as a pure photo-catalyst in the oxidation of formaldehyde by hydrogen peroxide. The other experimental precautions mentioned in the previous paper were also taken in this case.

Experimental.

Apparatus and experimental arrangement are same as in a previous paper. (*J. Indian Chem. Soc.*, 1929, **6**, 911).

First of all, it was observed whether there was any decomposition of formaldehyde only in ultra-violet rays. Formaldehyde was estimated by titrating with iodine and sodium thiosulphate (*vide* Plimmer, "Practical Organic and Biochemistry," p.85).

It will be seen from the following table that formaldehyde does not decompose in ultra-violet rays.

Table I.

Conc. of formaldehyde.	Time.	C.c. of thiosulphate≡3 c.c. $H{\cdot}CHO$ + 20 c.c. iodine sol.
0·1149 *M*	0 hrs.	29·9 c.c.
	2	29·9
	4	29·9
0·01149 *M*	0	29·5
	2	29·5
	4	29·45

Hydrogen peroxide (Merck's chemically pure "Perhydrol") in acid solution was then exposed to ultra-violet rays to see whether there was any decomposition. Kingzett's methods was adopted for the estimation of hydrogen peroxide.

Corning glass filter G.586 J (*vide* Teachnologic Papers of the Bureau of Standards, No. 148) was used for isolating the spectral region 430$\mu\mu$—330$\mu\mu$ in the violet and the ultra-violet. It was interposed between the reaction tube and the mercury lamp. With this glass filter, hydrogen peroxide in acid solution did not decompose.

Then a mixture of hydrogen peroxide, hydrochloric acid and formaldehyde was exposed to ultra-violet rays and Corning glass filter G.586 J interposed between reaction cell and mercury lamp. It will be seen from the following table that there is no decomposition.

Conc. of H·CHO.	Conc. of H_2O_2.	Conc. of HCl.	Time.	C.c. of thiosulphate ≡3 c. c. reaction mixture.
0·033 *M*	0·015 *M*	0·1*N*	0 min.	8·3 c.c.
			120	8·3
			180	8.3

Finally, a mixture of formaldehyde, hydrogen peroxide, hydrochloric acid and sodium tungstate was used. The hydrogen peroxide solution was freshly prepared before each day's experiment, as it decomposed in glass vessel after standing for some time. Radiations in the spectral region 430$\mu\mu$—330$\mu\mu$ have no action of hydrogen peroxide as such, but the ultra-violet light transmitted by this filter is very effective in bringing about the oxidation of formaldehyde by tungstic acid sol and hydrogen peroxide.

The reaction mixtures used in this investigation are given in the following tables. It will be noticed that the concentration of hydrochloric acid was never less than 0·075*N*. Sodium tungstate reacts with hydrochloric acid to form a sol according to the following equation:—

$$4Na_2WO_4 + 6HCl = Na_2O,\ 4WO_3 + 2NaCl + 3H_2O.$$

In our experiment, therefore, the molar concentration of tungstate was always less than two-thirds of the concentration of hydrochloric acid. The reaction mixtures were quite stable in the dark and no visible turbidity due to the coagulation of the tungstic acid sol occurred during the time of carrying out the experiments.

The hydrogen peroxide left over was estimated by Kingzett's method. In acid solution, the presence of formaldahyde does not affect the titration in the least.

That a mixture of formaldehyde, hydrogen peroxide, hydrochloric acid and sodium tungstate does not react in the dark, will be seen from the following table.

TABLE II.

Temp. of thermostat = 30°. Conc. of formaldehyde = 0·0287 *M*. Conc. of hydrogen peroxide = 0·02043 *M*. Conc. of sodium tungstate = 0·025 *M*. Conc. of hydrochloric acid = 0·0794 *N*. Conc. of thiosulphate = 0·01 *N*.

Time in min.	C.c. of thiosulphate ≡ 3 c.c. reaction mixture.
0	12·9 c.c.
120	12·9
240	12·9

The experimental results for different concentrations of formaldehyde and hydrogen peroxide are recorded in Table II*a*—II*c*.

TABLE II*a*.

	Conc. of CH_2O.	Conc. of H_2O_2.	Conc. of HCl.	Conc. of free HCl.	Conc. of tungstate.	k (unimolecular with respect to H_2O_2).
(*a*)	0·0287 *M*	0·01267 *M*	0·0794 *N*	0·0419 *N*	0·025 *M*	0·0026
(*b*)	,,	0·02043 *M*	,,	,,	,,	0·0025
(*c*)	,,	0·02290 *M*	,,	,,	,,	0·0024
(*d*)	,,	0·02585 *M*	,,	,,	,,	0·0020
(*e*)	,,	0·02710 *M*	,,	,,	,,	0·0010
(*f*)	,,	0·03452 *M*	,,	,,	,,	0·00083

TABLE II*b*.

(*a*)	0·0357 *M*	0·01590 *M*	0·0809 *N*	0·0434 *N*	0·025 *M*	0·0029
(*b*)	,,	0·02590 *M*	,,	,,	,,	0·0027
(*c*)	,,	0·02843 *M*	,,	,,	,,	0·0013
(*d*)	,,	0·04628 *M*	,,	,	,,	0·00049

TABLE IIc.

Conc. of CH_2O.	Conc. of H_2O_2.	Conc. of HCl.	Conc. of free HCl	Conc. of tungstate.	k (unimolecular with respect to H_2O_2).
(*a*) 0·0685 *M*	0·0199 *M*	0·0787 *N*	0·0412 *N*	0·025 *M*	0·0030
(*b*) ,,	0·0255 *M*	,,	,,	,,	0·0029
(*c*) ,,	0·0290 *M*	,,	,,	,,	0·0020
(*d*) ,,	0·0439 *M*	,,	,,	,,	0·00085

The experimental results given in Tables II(*a*), II(*b*) and II(*c*) are plotted graphically in Figure I. It will be noticed that the velocity constants diminish slowly at first, as the concentration of hydrogen peroxide increases. At about a concentration of hydrogen peroxide equivalent to the concentration of sodium tungstate, the curve suddenly shows a steep descent and then with further increase in the concentration of hydrogen peroxide becomes flat again.

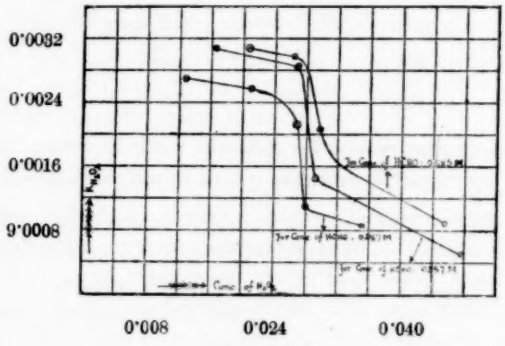

FIG. I.

As the concentration of formaldehyde increases, the curves are pushed further and further from the point of origin, the curves for higher concentration of formaldehyde lying above the curve for the lower concentration, but the nature of the curve remains the same. It is also to be noted that for higher concentrations of hydrogen peroxide—concentrations greater than 5·026*N*—the velocity of reaction becomes almost zeromolecular. Of course, when the initial concentration of hydrogen peroxide is large and the total change is a small fraction of the initial concentration, it is difficult to decide exactly whether a reaction is zeromolecular or unimolecular, but in this case, there is unmistakable evidence that the reaction, with large increase in the concentration of hydrogen peroxide tends to be zeromolecular.

Effect of Varying the Concentration of Formaldehyde.

TABLE III.

Temperature of thermostat = 32°.

Conc. of CH_2O.	Conc. of H_2O_2.	Conc. of HCl.	Conc. of free HCl.	Conc. of tungstate.	k.
(*a*) 0·0134 *M*	0·026 *M*	0·0787 *N*	0·0412 *N*	0·025 *M*	0·0011
(*b*) 0·0287 *M*	0·02585 *M*	0·0794 *N*	0·0419 *N*	,,	0·0020
(*c*) 0·0685 *M*	0·0255 *M*	0·0787 *N*	0·0412 *N*	,,	0·0029

TABLE IV.

Temperature of thermostat = 32°.

Conc. of CH_2O.	Conc. of H_2O_2.	Conc. of HCl.	Conc. of free HCl.	Conc. of tungstate.	k.
(*a*) 0·0287 *M*	0·02710 *M*	0·0794 *N*	0·0419 *N*	0·025 *M*	0·001
(*b*) 0·0357 *M*	0·02843 *M*	0·0809 *N*	0·0434 *N*	,,	0·0013
(*c*) 0·0685 *M*	0·02900 *M*	0·0787 *N*	0·0412 *N*	,,	0·002

When we plot graphically $1/k$ against $1/conc.\ of\ formaldehyde$, we see that there is a straight line (Fig. 2).

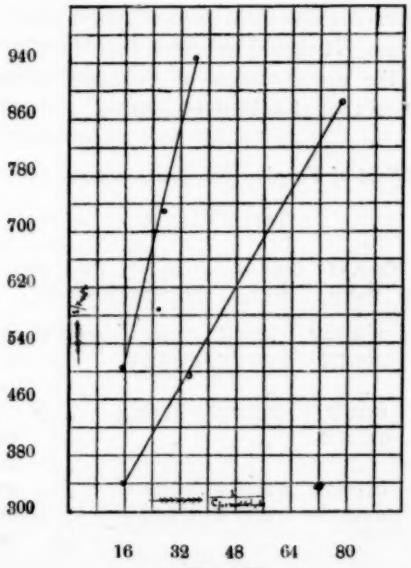

FIG. II.

Effect of Varying the Concentration of HCl.

TABLE V.

Temperature of thermostat = 32°.

Conc. of CH_2O.	Conc. of H_2O_2.	Conc. of HCl.	Conc. of free HCl.	Conc. of tungstate.	k.
0·0287 *M*	0·02585 *M*	0·0794 *N*	0·0419 *N*	0·025 *M*	0·002
0·0280 *M*	0·0255 *M*	0·2360 *N*	0·1990 *N*	,,	0·0011

It will be seen that the unimolecular constant almost varies inversely as the square root of the concentration of free hydrochloric acid.

Effect of Varying the Concentration of Sodium Tungstate.

TABLE VI.

Temperature of thermostat = 32°.

Conc. of CH_2O.	Conc. of H_2O_2.	Conc. of HCl.	Conc. of free HCl.	Conc. of tungstate.	k.
0·028 *M*	0·0255 *M*	0·236 *N*	0·1990 *N*	0·0250 *M*	0·0011
,,	0·0250 *M*	,,	0·2172 *N*	0·0125 *M*	0·00099
,,	,,	,,	0·2266 *N*	0·0063 *M*	0·00066
,,	,,	,,	0·2305 *N*	0·0037 *M*	0·00060

The volocity constant diminishes as the concentration of sodium tungstate diminishes. It should be noted that in the experiments described above, the concentration of hydrogen peroxide is either equal or greater than that of sodium tungstate.

Effect of Varying the Temperature.

TABLE VII.

Temp. of thermostat.	Conc. of CH_2O.	Conc. of H_2O_2.	Conc. of HCl.	Conc. of free HCl.	Conc. of tungstate.	k.	Temp. coeff. $= \frac{k_t + 10}{k_t}$
32°	0·0287*M*	0·03452*M*	0·0794 *N*	0·0419 *N*	0·025 *M*	0·00083	
37°	0·0280*M*	0·0357*M*	0·0787 *N*	0·0412 *N*	,,	0·00092	1·2
42° (calc.)	,,	,,	,,	,,	,,	0·0010	
32°	0·0685*M*	0·035*M*	0·0787 *N*	0·0412 *N*	,,	0·0018	
37°	,,	0·0357*M*	,,	,,	,,	0·0021	1·270
42° (calc.)	,,	,,	,,	,,	,,	0·0024	
32°	0·0287*M*	0·02043*M*	0·0794 *N*	0·0419 *N*	,,	0·0025	
37°	0·0280*M*	0·0207*M*	0·0787 *N*	0·0412 *N*	,,	0·0029	1·34
42° (calc.)	,,	,,	,,	,,	,,	0·0033	

The temperature coefficient is small, being of the order of 1·2—1·3.

Effect of Varying the Intensity of Radiation.

TABLE VIII.

Temperature of thermostat = 32°.

Intensity of radiation. (in ergs. per sq. cm. per sec.).	Conc. of CH_2O.	Conc. of H_2O_2.	Conc. of HCl.	Conc. of free HCl.	Conc. of tungstate.	k.
1512	0·0287 *M*	0·03452 *M*	0·0794 *N*	0·0419 *N*	0·025 *M*	0·00083
785	0·028 *M*	0·035 *M*	0·0787 *N*	0·0412 *N*	,,	0·00061
1512	0·028 *M*	0·0357 *M*	0·236 *N*	0·199 *N*	,,	0 00054
785	,,	0·035 *M*	,,	,,	,,	0·00051
1512	0·0685 *M*	0·035 *M*	0·0787 *N*	0·0412 *N*	,,	0·0018
785	,,	,,	,,	,,	,,	0·0013

It will be seen from Table VIII that for free acid strength 0·04*N*, the velocity constants vary as the square root of intensity of incident radiation; but when the concentration of free hydrochloric acid is large, the velocity constant varies only very slightly with increase in the intensity of radiation.

The intensity of ultra-violet radiations, absorbed by the reacting systems after passing through a Corning glass filter G.586 J and a rectangular quartz vessel filled with water at constant temperature was measured by a Moll thermopile and galvanometer. The quantum efficiencies are recorded in Table IX.

TABLE IX.

Quantum efficiency : calculated from	Composition of reaction mixture.	Quantum efficiency.
(1) *f* in Table II*a*	0·0287*M*-HCHO + 0·03452*M*-H_2O_2 + 0·0794 *N*-HCl + 0·025 *M*-tungstate.	3
(2) *d* ,,	0·02585*M*-H_2O_2. All other factors same as in (1).	4·7
(3) *b* in Table II*b*	0·0357*M*-HCHO + 0·0259*M*-H_2O_2 + 0·0809 *N*-HCl + 0·025 *M*-tungstate.	7·2
(4) *d* ,,	0·04628*M*-H_2O_2. All other factors same as in (3).	2·4
(5) *a* in Table III	0·0134 *M*-HCHO + 0·0260 *M*-H_2O_2 + 0·0787 *N*-HCl + 0·025 *M*-tungstate.	2·76
(6) *d* in Table IV	0·0685 *M*-HCHO + 0·0787 *N*HCl + 0·025 *M*-tungstate + 0·029 *M*-H_2O_2.	3·4

Discussion of Experimental Results.

Any mechanism of reaction that may be proposed for this photochemical oxidation should be in a position to explain the following facts:—

(1) The velocity of reaction with reference to hydrogen peroxide is monomolecular at lower concentrations of hydrogen peroxide, but tends to become zeromolecular as the initial concentration of hydrogen peroxide increases.

(2) With increase in the initial concentration of hydrogen peroxide keeping the concentration of sodium tungstate fixed at 0·025 *M*, the velocity constant slowly diminishes, but when a concentration of hydrogen peroxide, almost equal to that of sodium tungstate is reached, the velocity constant diminishes very rapidly (Fig. 1).

(3) The velocity constant is inversely proportional to the concentration of hydrogen ion.

(4) The velocity constant increases slightly as the concentration of formaldehyde is increased.

(5) Provided the concentration of hydrogen peroxide is equal to or greater than that of sodium tungstate, the velocity constant diminishes as the concentration of sodium tungstate diminishes.

(6) For smaller concentrations of free hydrochloric acid, the velocity constant varies as the square root of the intensity of incident radiation ; but for higher acid concentrations, the variation of velocity constant with intensity is much smaller.

(7) Two to seven molecules of formaldehyde undergo oxidation for each quantum of light absorbed.

(8) Temperature coefficient of the velocity of reaction is small.

It is obvious that the central feature of the reaction is indicated by the very rapid fall in the value of the velocity constant when the initial concentration of hydrogen peroxide becomes almost equivalent to that of sodium tungstate. The only possible satisfactory explanation of this remarkable fact lies in assuming that tungstic acid molecules combine with hydrogen peroxide to form a peroxide which does not exist as sol, but remains dissolved as a true solution. The molecule of this peroxide compound may, like molecules of hydrogen peroxide, react with formaldehyde to give rise to formic acid and behave also as molecules of hydrogen peroxide in the process of iodometric titration. It is only the sol of tungstic acid which presents a

photo-sensitive surface, on which may be fixed by adsorption a molecule of hydrogen peroxide, or a molecule of pertungstic acid, which in their turn, react with formaldehyde under stimulus of light. The evidence in favour of the formation of pertungstic acid molecule, by reaction of tungstic acid with hydrogen peroxide, has been furnished by Pissarjewsky (*Z. physikal. Chem.*, **43**, 166). He determined the distribution of hydrogen peroxide between ether and an aqueous solution of sodium tungstate and sulphuric acid and concluded that a considerable amount of hydrogen peroxide remained combined with tungstic acid in aqueous solution. We, therefore, postulate that a molecule of hydrogen peroxide combines with a molecule of sodium tungstate to form a molecule of pertungstic acid.

$$H_2O_2 + H_2WO_4 + (\text{HCl in excess}) \rightleftarrows H_2WO_4.H_2O_2$$

If the dissociation constant k' of the pertungstic acid is small, then it follows that—

(*a*) For $C_{H_2WO_4} > C_{H_2O_2}$

the concentration of tungstic acid as such $= C_{H_2WO_4} - C_{H_2O_2}$.

(*b*) For $C_{H_2WO_4} = C_{H_2O_2}$

the concentration of tungstic acid $= \sqrt{k'.C_{H_2O_2}}$.

(*c*) For $C_{H_2O_2} > C_{H_2WO_4}$

the concentration of tungstic acid $= \dfrac{k'.C_{H_2WO_4}}{C_{H_2O_2} - C_{H_2WO_4}}$.

Since the value of k' is small, it is clear that for a definite initial concentration of tungstic acid, the quantity of tungstic acid existing in colloidal state will continually diminish as the concentration of hydrogen peroxide is increased, but at values of equivalent concentration, the diminution will be extremely rapid. Now, on the very reasonable assumption that it is the tungstic acid sol that is photo-sensitive, we are in a position to explain the observed sudden diminution of the velocity constant, when the concentration of hydrogen peroxide becomes equivalent to that of sodium tungstate.

Beyond this transition point, the concentration of tungstic acid existing as such, becomes very small and its rate of diminution with further increase in the concentration of hydrogen peroxide becomes much less, and the curve of velocity constants becomes necessarily flat again.

We are also now in a position to explain the other features of this reaction. It is well-known that particles of a tungstic acid sol are negatively charged and hydrogen ions will therefore be electrically adsorbed on the surface. According to Mukherjee (*Trans. Farad. Soc.*, 1921, **16**, 103) the fraction θ of the original charge on the surface not neutralised by adsorption of monovalent ions is given by the following equation—

$$k_2C\theta^2+\theta-1=0$$

where C is the concentration of monovalent ion. Now, if θ be small compared with unity, that is, if the neutralisation of charge is almost complete, which we may expect when the concentration of hydrogen ion is not too small,

$$\theta^2=\frac{1}{k_2C} \qquad \text{or} \quad \theta=\frac{k_3}{\sqrt{C_H}}.$$

If θ is the fraction of the charge not neutralised by hydrogen ions, it follows that θ also represents the fraction of the total surface of sol particles, which remains available for adsorption by other molecular species. We have already postulated that molecules of hydrogen peroxide or pertungstic acid can be adsorbed on the surface of tungstic acid sol particles. The amount of adsorption complex so formed will be proportional to the concentration of peroxide (free hydrogen peroxide + peroxide of tungstic acid) and the free surface or

$$\theta_1 \text{ (fraction of surface covered with peroxide)} = k_3.C_{H_2O_2}.\frac{k_2}{\sqrt{C_H}}.$$

This relation is true only when the concentration of peroxide is not very large compared with the concentration of the sol. If the concentration of peroxide is very large, then the whole of the available surface θ will be covered with peroxide and we shall be dealing with a saturated surface.

$$\text{Here} \quad \theta_1=\theta=\frac{k_3}{\sqrt{C_H}}.$$

The elementary spaces of the surface covered with hydrogen peroxide or pertungstic acid get activated under the stimulus of radiation and may oxidise a molecule of formaldehyde which happens to collide against this surface during its life-period of excitation. If τ be the life-period of this excited peroxide spaces, and T be the interval between two successive collisions of formaldehyde molecules on the same peroxide space, the velocity of oxidation of formaldehyde will be given by the following equations—the intensity of effective radiation remaining constant.

$$\frac{dx}{dt} = k_4 . \frac{\tau}{T+\tau} . \theta_1 .$$

The interval between two successive collisions of the formaldehyde molecules against the peroxide surface will be inversely proportional to the concentration of formaldehyde.

Hence

$$\frac{dx}{dt} = \frac{\tau}{\frac{A}{C_{\text{formaldehyde}}} + \tau} . k_4 . k_3 . k_2 . \frac{C_{H_2O_2}}{\sqrt{C_H}} .$$ for lower conc. of H_2O_2.

and $$\frac{dx}{dt} = \frac{\tau}{\frac{A}{C_{\text{formaldehyde}}} + \tau} . k_4 . \frac{k_3}{\sqrt{C_H}}$$ for very large conc. of H_2O_2.

If T or $A/C_{\text{formaldehyde}}$ be small compared with τ,

$$\frac{dx}{dt} = k_5 . \frac{C_{H_2O_2}}{\sqrt{C_H}}$$ for lower conc. of H_2O_2,

and $$\frac{dx}{dt} = \frac{k_6}{\sqrt{C_H}}$$ for large conc. of H_2O_2.

That is, for lower concentration of hydrogen peroxide, we have a unimolecular reaction whose velocity varies inversely as the square root of concentration of hydrogen. For large concentrations of hydrogen peroxide, the reaction tends to be zeromolecular.

It will also be noticed that the function $\frac{\tau}{\frac{A}{C_{\text{formaldehyde}}} + \tau}$

is included in the values of k_5 or k_6 and $1/k_5$ or $1/k_6$ will therefore, include the expression,

$$\frac{\tau + \frac{A}{C_{\text{formaldehede}}}}{\tau} \quad \text{or} \quad 1 + \frac{A}{\tau} = \frac{1}{C_{\text{formaldehyde}}}.$$

It is therefore to be expected, that other conditions remaining the same, the inverse of velocity constant plotted against the inverse of the concentration of formaldehyde should be a straight line. This has been found approximately to be the case.

The values (between two and seven) for quantum efficiency of the reaction, indicate that there exists a chain mechanism for the reaction, but that the length of the chain is quite small. The small temperature coefficient of the reaction also indicates that the nature of the dark reaction chains following the primary photochemical process is fairly simple. It is, however, premature at this stage to attempt to postulate the exact nature of the chain mechanism.

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A Preliminary Note on the Homology of BeF_4'' and SO''_4 Ions from Chemical, Structural and Crystallograpic Points of View.

By Pulin Bihari Sarkar and Nirmalendunath Ray.

Complex salts are generally divided according to their degree of stability into three classes, *viz.*,

(1) Perfect complexes as are exhibited by the less electropositive elements such as Pt, Co, Rh, Ir, etc., which are not at all dissociated into their constituents.

(2) Imperfect complexes, as shown by chromium, which partially dissociate.

(3) The double salts which undergo complete dissociation in aqueous solution, *e.g.*, $2KCl, SnCl_4$.

Such a classification of the complex ions actually presents serious difficulties on account of the transition which leads us insensibly from perfect complex ions to complex ions disintegrating in solution in such a way that the analytical characters cease to be the discriminating guide. In such cases the analogy cannot be searched for in the properties of the solution. It is therefore to the properties of the solid salts that recourse is to be taken for establishing the analogy. The similarity of crystalline form is of course one of the most valuable properties for consideration. Such an analogy may, however, be accidental. Several concordant presumptions are necessary for establishing the analogy. Amongst the necessary coincidences the identity of type is one of the essentials. Simple analogy of formula alone is of no value. If the compounds of analogous formulae are isomorphous in appearance it remains still to be assured that the conditions of " real " isomorphism are satisfied. The word " real " implies an analogy much more profound than that of simple exterior form. One of the characters of real isomorphism is the formation of mixed crystals, which can at least within certain limits, admit of infinite compositions. The crystallisation in all proportions is a particular and extreme case of the preceding. When this character accompanies an absolute identity of form, the isomorphism is perfect. But this conception has its limitations. In fact

the crystals of two isomorphous salts are never rigorously identical, the corresponding angles present always slight differences. That isomorphism reveals most profound chemical analogies is best exemplified by the family of the rare earths. Their salts of the same type have always the same crystalline form and they form mixed crystals in all proportions.

It is to be assumed that there are not only homologous elements but there are also homologous radicles. A very well-known example is furnished by ammonium and potassium ions. When certain elements or radicles can be substituted totally or partially in a variety of salts without disturbing the conditions for " real " isomorphism, the chemical homology of these elements or radicles remains indisputable.

One of the essential conditions of syncrystallisation of two perfectly isomorphous crystals is the quasi-equality of molecular volumes.

A search for literature about the double fluorides of beryllium reveals the existence of salts of the type MF, BeF_2 and 2MF, BeF_2 (where M=K, Na or Am). Up till now no investigation has been carried out to prove whether they form true double salts or constitute a complex ion. It has been found that on adding ammonia to a moderately concentrated solution of potassium beryllium fluoride (2KF, BeF_2), beryllium is only partially precipitated. Moreover, with a very concentrated solution of ammonium beryllium fluoride ($2NH_4F$, BeF_2, which is much more soluble than the potassium salt) the precipitation with ammonia cannot be effected and the precipitate of beryllium hydroxide can be made to appear on dilution of the ammoniacal solution. These observations amply justify the assumption that beryllium in solutions of these double fluoride is a constituent of a complex ion. This was definitely proved by a transport experiment. On electrolysing a concentrated solution of potassium beryllium fluoride a gradual and marked increase in the concentration of beryllium at the anode was observed although part of the beryllium was precipitated as hydroxide at the cathode. The same observation was also made with an approximately normal solution of ammonium beryllium fluoride. The details will be published later on. It is therefore assumed that in the aqueous solution of potassium beryllium fluoride or ammonium beryllium fluoride BeF_4''-ion exists though partially dissociated into its constituents $Be^{\cdot\cdot}$ and $4F'$. (A study of the dissociation constant of this complex ion is in progress.)

Now BeF_4'' is iscsteric and isoelectric with SO_4'' each having 5 atoms and 32 peripheric electrons the covalences of Be and S being 4 in each case. The structure of the ions may be represented thus,

each atom having assumed the structure of neon. Proceeding with Langmuir's theory of octets a conclusion may be drawn that these isoelectric isosteres should exhibit close relationship in physical and chemical properties. Molecular volumes of the ammonium salts of these complex ions have been determined and found to be very close (mol. vol. of $2NH_4F$, $BeF_2 = 71{\cdot}9_{30}°$ and of $(NH_4)_2SO_4 = 70{\cdot}7_{30}°$). In fact Barker (*J. Chem. Soc.*, 1912, **102**, 484) cited in his examples of unexplained isomorphism the cases of potassium sulphate and potassium beryllium fluoride, their crystallographic constant as given by him approaching each other very closely:—

	a	*b*	*c*
K_2BeF_4	0·5708	: 1 :	0·7395
K_2SO_4	0·5727	: 1 :	0·7418

Goldschmidt (*Trans. Faraday Soc.*, 1929, **25**, 282) has recently found the following ionic radii:

$S^{\cdots\cdots}$	...	0·32 A.U.	O''	...	1·32 A.U.
$Be^{\cdot\cdot}$	...	0·34 A.U.	F'	...	1·33 A.U.

After having determined the molecular volumes of ammonium beryllium fluoride and ammonium sulphate we prepared a series of mixed crystals of the above two salts. Assuming syncrystallisation of the two chemical species—which entails equality of molecular co-efficients, thermic and elastic—as the best criterion of chemical analogy we have prepared the following double salts:—

$(NH_4)_2BeF_4,NiSO_4,6H_2O$.	$(NH_4)_2BeF_4,MnSO_4,6H_2O$.
„ $CoSO_4$ „	„ $MgSO_4$ „
„ $ZnSO_4$ „	„ $CdSO_4$ „
„ $FeSO_4$ „	

which are monoclinic and perfectly isomorphous with the well-known double sulphates of ammonium and those of magnesium family of elements studied by Locke. (*Amer. J. Sci.*, 1902, **27**, 455). With potassium beryllium fluoride the following isomorphous series of double salts have also been prepared.

$K_2BeF_4, NiSO_4, 6H_2O$.

" $ZnSO_4$ "

" $CoSO_4$ "

" $CuSO_4$ "

In the above examples BeF_4'' has partially replaced SO_4''. A third series of double salts have been prepared in which the SO_4-ions have been completely replaced, *e.g.*, Am_2BeF_4, $NiBeF_4$, $6H_2O$ perfectly isomorphous with the aforesaid series. Further corroborative evidence of the analogy is afforded by the preparation of the fourth series, *viz.*, the alums, *e.g.*, $Al_2(SO_4)_3$, Am_2BeF_4, $24H_2O$. Moreover, a simple salt $NiBeF_4$, $7H_2O$ analogous to $NiSO_4$, $7H_2O$ has also been prepared.

As it was expected that the two complex ions BeF_4'' and SO_4'' will show futher chemical similarity in respect of various other salts soluble or insoluble, an attempt was made to prepare the fluoberyllates of the metals of the alkaline earths. Now, as the complex ion BeF_4 in aqueous solution is in mobile equilibrium with its ions, $BeF_4'' \rightleftarrows Be'' + 4F'$, we cannot use wet method to verify the above hypothesis. By fusing ammonium beryllium fluoride with anhydrous barium chloride at high temperature we have been able to isolate the compound $BaBeF_4$ which correspond to $BaSO_4$ and is equally insoluble in water and acids. It is thus evident that a close chemical analogy between two negative ions composed of elements belonging to widely different groups in the periodic table is possible. A detailed account of the investigations summarised above will appear in a series of subsequent communications.

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Studies in Silicic Acid Gels. Part III. Effect of Non-electrolytes on the Time of Setting of the Gel-forming Mixtures.

By Mata Prasad and R. R. Hattiangadi.

It has been shown in the previous communication that when solutions of acidic ammonium acetate or acetic acid and sodium silicate are mixed together, a colloidal solution of silicic acid is first formed in the mixture; the charge on the colloidal particles is positive or negative according to the acidic or alkaline nature of the medium. The gel is probably formed by the coagulation of the colloidal solution.

It is well known that non-electrolytes cause the coagulation of many negatively and positively charged colloidal solutions and also exert a retarding or accelerating influence on the coagulation of sols by electrolytes. Gel-forming mixtures contain an undialyzed sol of silicic acid (*cf.* Part II) and the addition of non-electrolytes to these mixtures may influence the coagulation of the sol by the electrolytes present in the mixture.

The present investigation was, therefore, undertaken to examine the behaviour of non-electrolytes on the time of setting of the gel-forming mixtures. The silicic acid gels studied in this investigation have been prepared by Bhatnagar and Mathur's method (*Kolloid. Z.*, 1922, **30**, 368) as well as by mixing solution of sodium silicate with various organic and inorganic acids.

Experimental.

A stock solution of sodium silicate (Na_2O, $2SiO_2$) was prepared as described in Part I (*J. Indian Chem. Soc.*, 1929, **6**, 653) and the 4 per cent. solutions, used throughout this investigation, were prepared from it by dilution, each time any series of observations

were made. A solution of 4 per cent. silica content was titrated with 0·66 *N*-acids. In all the experiments described in this paper, gels were prepared with acids above or below this concentration. Merck's pure acids were used throughout and were carefully standardised.

The effect of pyridine, alcohols and acetone has been studied. The effect of pyridine has been studied more elaborately than that of other non-electrolytes because of its interesting behaviour.

Solutions of sodium silicate containing the non-electrolytes and of acids or of acidic ammonium acetate were mixed together by pouring the contents from one test-tube to another. But it was found that solutions were not thoroughly mixed in this way; often local flocculation took place and a uniform gel was not obtained. To overcome this difficulty the device described below was used.

A short limb of a glass tube was fused to a longer limb of glass at an acute angle. The two solutions were introduced into the two limbs and the open end was closed by a rubber cork. The contents were mixed by a rapidly inverting the arrangement a number of times. The stop-watch was started simultaneously with the mixing.

Solutions after thorough mixing were transfered to the cell and the deflections of the galvanometer were noted at different intervals of time. The time of the setting of the gel was determined from the time-deflection curves in the manner pointed out in Part I. (*loc. cit.*)

Effect of Pyridine.

Different amounts of pyridine were added to 5 c.c. of the sodium silicate solution and this was mixed with 5 c.c. of varying concentrations of ammonium acetate and hydrochloric acid in the manner described above. In each of these experiments the total volume of the mixture was therefore more than 10 c.c. The dilution factor was not taken into consideration as the effect of the added non-electrolyte was predominantly coagulating.

The results obtained are described in the following tables. The symbols employed repesent

Q = c.c. of pyridine added to 10 c.c. of the mixture;
t = time of setting of the gel ;
A = scattering of light, D_i-D_t (where D_i and D_t are the deflections initially and at the time t) in terms of deflections in mm. of the galvanometer.

TABLE I.

Concentration of NH_4Ac = 5 per cent.

Reaction alkaline.

Q ...	0	0·1	0·3	0·6	1·0
t ...	7	6	4½	3½	3
A ...	19	21	22	22	28

TABLE II.

Concentration of NH_4Ac = 20 per cent.

Reaction acidic.

0	0·2	0·6
26	7	¼ min.
7	24	Ppt.

TABLE III.

Reaction alkaline.

0·372*N*-HCl.			0·43*N*-HCl.			0·5*N*-HCl.			0·59*N*-HCl.		
Q	*t*	*A*	*Q*	*t*	*A*	*Q*	*t*	*A*	*Q*	*t*	*A*
1·0	26 min.	43	1·0	7 min.	42	1·0	5 min.	30	1·0	6½ min.	17
1·2	8	53	1·2	3	49	1·2	2½	33	1·2	3½	23
		Ppt.			Ppt.	2·0	½	62	2·0	2	24

TABLE IV.

Reaction acidic.

0·75*N*-HCl.			1·53*N*-HCl.		
Q	*t*	*A*	*Q*	*t*	*A*
0	8 days	—		18 days	
0·05	12 min.	15	0·4	37 min.	17
0·1	6 ,,	24	0·5	13	29
0·2	3 ,,	37	0·6	9	44
0·3	10 sec.	70	0·7	3	65
0·4		Ppt.	0·8		Ppt.

It will be seen from Tables I-IV that pyridine has got a marked coagulating power both in the acid and the alkaline media. The time of setting of the gel decreases as the concentration of pyridine in the mixture is increased, till after a certain concentration no gel but a

mere flocculent precipitate is obtained. The increase in the quantity of pyridine in the mixture also increases the opacity of the gel.

It will also be seen from Table III that with the same quantity of pyridine the opacity of the gels formed from alkaline mixtures increases as the alkalinity of the mixtures is increased. It has been shown in Part I that in alkaline mixtures the gels obtained have larger molecular aggregates than in the acidic ones. It, therefore, appears that if the process of gelation is accelerated by a coagulant, the tendency of the alkaline mixture will be to give precipitates and not gels.

In the acid media on the other hand, the same amount of pyridine increases the time of setting as well as the transparency, with an increase in the acidity of the mixture.

Comparative Effect of Pyridine on the Setting of Mixtures of Solutions of Sodium Silicate and Organic and Inorganic Acids.

The comparative effect of pyridine on the setting of silicic acid gel from mixtures of sodium silicate solutions and nitric, hydrochloric and sulphuric acids and acetic, trichloracetic, formic tartaric and citric acids from alkaline and acidic mixtures was then studied. The strengths of acids used in the acid and alkaline region were 1·46*N* and 0·486*N* respectively.

The time of setting with these mixtures, containing varying amounts of pyridine, was measured from the time-deflection curves. The results obtained are given in the following tables. The symbols used carry the same meaning as before.

TABLE V.

Reaction alkaline.

Q ...	0	0·8		1·0		1·2		2·0	
Acids.	*t*	*t* (min.)	*A*	*t* (min.)	*A*	*t* (min.)	*A*	*t* (min.)	*A*
Sulphuric ...	4 days	—	—	13	20·5	12	28	1	50
Hydrochloric ...	24 hrs.	12	24	7	30	3	38		Ppt.
Nitric ...	nearly ,,	12	25	6	31	2½	43		,,

TABLE VI.

Reaction acidic.

Q ...	0	0·4		0·5		0·7	
Acids.	*t*	*t* (min.)	*A*	*t* (min.)	*A*	*t* (min.)	*A*
Sulphuric ...	15 days	9	21	6	32		Ppt.
Hydrochloric	16	10	19	7	27		,,
Nitric ...	21	13	14	8	27		,,

TABLE VII.

Reaction alkaline.

Q ...	0	0·8		1·0		1·2		2·0	
Acids.	*t*	*t* (min.)	*A*	*t* (min).	*A*	*t* (min.)	*A*	*t* (min.)	*A*
Trichloracetic ...	6 hrs.	8	42	3	48	1¼	60	Ppt. in 30 sec.	
Acetic ...	7	8	29	3½	32	2½	38	,, ,, ,, ,,	
Formic ...	—	9	27	4½	30	3	36	,, ,, 40 ,,	
Tartaric ...	48	30	19	13	21	8	24	1	61
Citric ...	4 days			33	17	13	23	3	39

TABLE VIII.

Reaction acidic.

Q ...	0	0·4		0·5		0·7
Acids.	*t*	*t* (min.)	*A*	*t* (min.)	*A*	
Citric ...	12 hrs.	5½	42	2	60	Ppt. in 15 sec.
Acetic ...	18 ,,	6½	35·5	3½	58	,, ,, 30 ,,
Tartaric ...	3 days	13	23	6½	37	Almost a stiff gel.
Trichloracetic ...	15 ,,	7	29	4	47·5	Ppt. in 45 sec.
Formic ...	—	13	25	6½	35	Almost a stiff gel.

It will be seen from Tables V-VIII that the effect of pyridine in all cases is one of coagulation. The order in which the time of setting is brought about by the same concentrations of mineral acids, with the same quantity of pyridine is sulphuric > hydrochloric > nitric in the acid and nearly nitric $\geq$ hydrochloric $\geq$ sulphuric in the alkaline one.

The same order is obtained with corresponding mixtures containing no pyridine in them. It is interesting to observe that the order of the acids obtained in the acid region is the order of their ionising power. It is to be expected, therefore, that the most highly ionised acid will normally delay the time of setting most. In the alkaline region the reverse order will be obtained.

With organic acids and pyridine the following order of behaviour is obtained in the acid and alkaline media respectively.

Citric $\geq$ Acetic $\geq$ Trichloracetic $\geq$ Formic $\geq$ Tartaric;

Trichloracetic $\geq$ Acetic $\geq$ Formic $\geq$ Tartaric $\geq$ Citric.

The same order has not been observed in the corresponding mixtures containing no pyridine in them.

The order of behaviour of the acids in the latter case is the same as that obtained by Holmes (*J. Phys. Chem.*, 1918, **22**, 510) who worked chiefly with acid mixtures and concluded that the time of setting is partly dependent upon the number of hydrogen ions present in the mixture and suggested that the influence of ions other than the hydrogen ions on the setting of the gels may be considerable. The latter suggestion has been borne out in the prssent case by the behaviour of sulphuric acid in the alkaline region, as it takes a comparatively long time to bring about the setting, and by other slight abnormalities in the behaviour of the organic acids.

Effect of Alcohols and Acetone.

The effect of methyl, ethyl, and propyl alcohols and acetone on the time of setting of the gel-forming mixtures prepared from acidic ammonium acetate and acetic acid was next studied.

5 C.c. of ammonium acetate of double the strength required for the experiment were mixed with twice the required amount

of alcohols or acetone and the total volume was carefully made up to 10 c.c. by the addition of distilled water. 5 C.c. of this mxture were mixed with 5 c.c. of the four per cent. solution of sodium silicate in the manner already described. As sodium silicate is sparingly soluble in alcohols or acetone, higher concentrations of these substances could not be used. The time of setting with ammonium acetate was measured from the time-deflection curves and with acetic acid by Fleming's method.

The results obtained are given in the following tables:—
Q_1*=c.c. of alcohol or acetone contained in 10 c.c. of the gel-forming mixtures.

TABLE IX.

Concentration of NH_4Ac=5 per cent.

Reaction alkaline.

Q_1	CH_3OH		C_2H_5OH		C_3H_7OH	
	t (mins.)	*A*	*t* (mins.)	*A*	*t* (min.)	*A*
0	6½	19	6½	19	6½	19
0·1	—	—	4½	20	3	20
0·25	4½	21	3½	21	2	22
0·5	3½	23	2½	24	1½	26
1·0	1½	26	35 sec.	38	15 sec.	50
2·0	½	40	—	—	—	—

TABLE X.

Reaction acidic.

Conc. of NH_4Ac=16·75 per cent.					Conc. of NH_4Ac=20 per cent.		
Q_1*	C_2H_5OH		C_3H_7OH		Q_1	CH_3OH	
	t (min.)	*A*	*t* (min.)	*A*		*t* (min.)	*A*
0	15	10	15	10	0	22	7
0·5	20	6	20	7	0·25	25	7
1·0	—	—	22	6·5	1·0	36	5
1·5	—	—	26	6	2·0	45	4

TABLE XI.

Concentration of acetic acid = 0·486*N*.

Reaction alkaline.

Q^*	CH_3OH	C_2H_5OH	C_3H_7OH
	t	*t*	*t*
0	7 hrs.	7 hrs.	7 hrs.
0·25	—	32 min.	29 min.
0·5	37 min.	8½ ,,	6½ ,,
1·0	5 ,,	50 sec.	35 sec.
1·5	2 ,,	5 ,,	4 ,,
2·0	Ppt.	Ppt.	Ppt.

TABLE XII.

Concentration of acetic acid = 0·82*N*

Reaction Acidic.

Q_1^*	CH_3OH	C_2H_5OH	C_3H_7OH
	t	*t*	*t*
0	55 (min.)	55 (min.)	55 (min.)
0·5	71	88	88
1·0	—	125	115
2·0	—	180	—
2·5	155	—	—

TABLE XIII.

Strength of NH_4Ac.	Reaction.	Q_1^* 0·25		0·5		1·0	
		t (min.)	*A*	*t* (min.)	*A*	*t* (min.)	*A*
16·75%	Acidic	14	7	15	7	22	6
4·0%	Alkaline	12	16	5	20	1	40

TABLE XIV.

Q_1^*	0·75*N*-NH_4Ac. Reaction acidic. *t*	Q_1^*	0·486*N*-HAc. Reaction alkaline. *t*
0	9½ min.	0	7 hrs.
0·5	19½	0·25	36 min.
1·0	30	1·0	1 ,,
2·0	62	1·5	7 sec.

It will be seen from the foregoing tables that increasing quantities of alcohol and acetone in the alkaline region not only decrease the time of setting but also increase the opacity of the gels.

The coagulating power of the alcohols increase with the increase in the CH_2 groups, that is $C_3H_7OH > C_2H_5OH > CH_3OH$. Acetone has about the same coagulating action as ethyl alcohol.

When the gel-forming mixtures are even slightly acidic, alcohols as well as acetone act as protective agents and the time of setting is considerably delayed in their presence. The transparency of the gels is not much affected but in some cases a tendency to make them slightly more transparent has been observed.

Effect of Non-electrolytes on the Dialysed Sol of Silicic Acid.

Thomas Graham (*J. Chem. Soc.*, 1864, **17**, 321) found that alcohols, syrup of sugar and glycerine were among the inactive diluents of the pure sol of silicic acid. Pappada (*Gazzetta*, 1905, *i*, **35**, 78, 86; *J. Chem. Soc., Abs.*, 1905, *ii*, **88**, 387) found that alcohols, glycol, sucrose and many other sugars had neither any coagulant action on colloidal silica nor exerted any retarding influence on substances which cause coagulation.

The effect of pyridine, alcohols and acetone was examined on the pure sol of silicic acid, prepared by dialysing a mixture of sodium silicate and hydrochloric acid, and it was found that these substances did not coagulate the sol. The effect of these substances was then examined on the pure sol made alkaline and acidic by the addition of sodium hydroxide and hydrochloric acid respectively. The results obtained are given in the following tables.

TABLE XV.

	Acid sol.	Alkaline sol.
Methyl alcohol	No action	Immediate coagulation.
Ethyl alcohol	,,	,,
Propyl alcohol	,,	,,
Acetone	,,	,,
Pyridine	,,	,,

Discussion of Results.

The behaviour of non-electrolytes on the setting of the silicic acid gel, when examined with reference to the nature of the medium in which it is formed, shows that there are two distinct effects: (*i*) That in an alkaline medium in which the colloidal particles of silicic acid carry a negative charge, the addition of the non-electrolytes decreases the time of setting or hastens the coagulation. (*ii*) That in a moderately acid medium where the particles are positively charged, the effect is to increase the time of setting or to exert a protective

influence on the colloidal particles. Pyridine is an exception to the above generalisation in that it hastens coagulation even in moderately acid mixtures.

The results obtained on the pure sol of silicic acid in the acid and alkaline media also indicate that the coagulation of the negatively charged sol takes place immediately by the addition of the non-electrolytes but the positive sol cannot be coagulated again, with the exception of pyridine. These results are similar to those of Klein (*Kolloid Z.*, 1921, **29**, 247) who has found that negatively charged sols of arsenious sulphide, gold, silica and ferric oxide are agglomerated in part by alcohols whereas positively charged ferric oxide and silica are not.

The abnormalities observed above, both with the dialysed and the undialysed sols of silicic acid, cannot be explained on the diminution of the dielectric constant of the mixture and hence on the change in the density of the charge carried by the colloid particles, except that influences are all specific. Kruyt and van Duin (*Koll. Chem. Beihefte.*, 1914, **5**, 287) were similarly unable to account for the fact that the same non-electrolyte stabilised a sol towards certain electrolytes and sensitised towards others.

Billitzer (*Z. physikal. Chem.*, 1903, **45**, 312) found that a negatively charged platinum sol could be sensitised, discharged or even charged into a positive sol by the addition of suitable amounts of alcohol. It is probable in the present case, that the alcohols and acetone stabilise the positively charged silicic acid by increasing the density of the charge, though this point cannot be emphasised, in view of the scanty data available on this subject. Besides, the electric charge on the particles is not the only factor exerting an influence upon the probability of adhesion in the case of lyophilic sols and emulsoids. The electric charge of sols of agar-agar or gelatine can be taken away fully without causing the least indication of coagulation (*cf.* Kruyt and de Jong, *Z. physikal. Chem.*, 1922, **100**, 250; de Jong, *Rec. trav. chim.*, 1924, **43**, 189). The stability of these sols is maintained by the hydration of the colloid particles. The influence of hydration may also be an important factor on the stability of the highly hydrated positively charged particles of silicic acid in the acid medium, without prejudice, however, to the coagulating effect of the alcohols on the negatively charged particles, where other factors are evidently at work.

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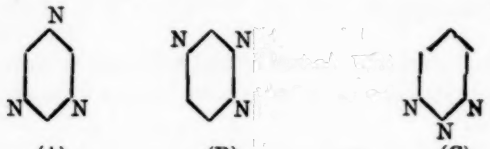
Syntheses in the Triazine Series.

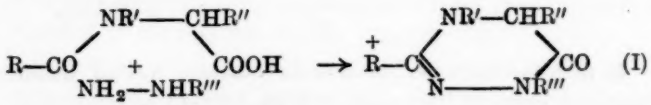
By Manmohan Sen.

Of the three possible types of triazines A, B, and C, type B seems to have been very little studied.



(A) (B) (C)

Few derivatives of this type (unsymmetrical α-triazine) are known. Besides none of the methods so far adopted for synthesising these simple rings is of wide applicability and almost all of them suffer from the disadvantage that the starting materials are difficult to obtain. In the present paper some unsymmetrical α-triazines have been synthesised and their properties studied. The synthesis was effected from such simple materials as hydrazines and acyl glycines in the manner of the syntheses of pyrazolones (Knorr, *Annalen*, 1887, **238**, 137) and of pyrrodiazolones (Andreocci, *Gazzetta*, 1890, **19**. 448) from hydrazines and β-ketonic esters and acyl urethanes respectively.



(I)

The method is expected to be one of wide applicability as by varying R, R′, R″ and R‴ a large number of triazines can be obtained.

The condensations were brought about by heating molecular proportions of the reactants in alcoholic solutions on the water-bath for 6 to 8 hours. Phenylhydrazine reacted smoothly with acetyl

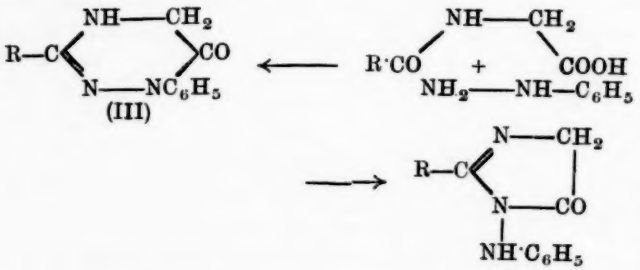
phenylglycine, acetyl-*o*-tolylglycine and acetyl-α-naphthylglycine. The products are all insoluble in both dilute and concentrated alkali solutions showing that they have no acidic properties. Dilute acids too have no action. They dissolve, however, in concentrated hydrochloric acid but are precipitated unchanged on dilution with water. They are, therefore, very weak bases. With concentrated sulphuric acid they form bright rose-red solutions.

Efforts to synthesise these triazines from acyl hydrazines and glycines met with indifferent success.

(II)

Acetylphenylhydrazine (symmetrical) could not be made to react with either phenylglycine or its ethyl ester though a variety of ways were employed.

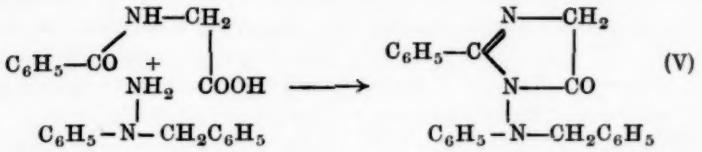
Acyl derivatives of unsubstituted glycines (hippuric acid and acetylglycine) were next made use of to note if a triazine or an iminazolone or a mixture of both would result, as in these cases there is the chance of the formation of both.



(IV)

In both the cases the compounds obtained melted indifferently even after repeated fractionations from different solvents, that from hippuric acid melting between 178 and 186°, and that from acetyl glycine between 200 and 206°. The analytical results tallied closely, however, with those demanded by compounds obtainable from the reactants by elimination of two molecules of water. This showed clearly that in these two cases intimate mixtures of triazines and iminazolones were being formed. The presence of the iminazolones

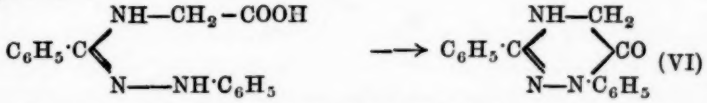
has been proved indirectly by condensing hippuric acid with unsymmetrical phenylbenzyl hydrazine under identical conditions.



(V)

The expected iminazolone was obtained in good yield thus proving the full possibility of the formation of an iminazolone under these conditions.

All efforts at separation having failed attempts were next made to arrive at the triazines by way of the intermediate phenylhydrazones.



(VI)

From phenylhydrazine and hippuric acid Scheiber and Reckleben (*Ber.*, 1913, **46**, 2419) had obtained hippuryl hydrazide $C_6H_5CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5$ (m.p. 184°). Here hippuric acid was heated in aqueous solution with phenylhydrazine hydrochloride and sodium acetate when the desired intermediate phenylhydrazone (m.p. 134°) was formed, though in poor yield. It was soluble in alkalis, showing the presence of a carboxyl group. For ring-closure this was heated at a temperature a few degrees above its melting point. On crystallising however the same mixture of triazine and iminazolone with the same indifferent melting point was obtained. This shows that the hydrazidine skeleton is tautomeric like amidines. It was observed that on longer heating the final product was formed along with the intermediate phenylhydrazone from which it was separated by washing with alkali.

It may be noted here that with benzoyl glycines the yield was invariably greater than with acetyl glycines, thus indicating the influence of the phenyl group on the adjacent carbonyl group.

Experimental.

Acetylphenylglycine.—Phenylglycine was obtained by heating one molecule of monochloroacetic acid with two molecules of aniline and water on the water-bath for two hours (*J. Chem. Soc.*, 1905, **87**,

438) and was acetylated by heating with acetic anhydride (*Ber.*, 1892, **25**, 2270).

Condensation with Phenylhydrazine: *Formation of* 2:5-*Diphenyl*-6-*methyl*-3-*ketotetrahydro*-α-*triazine*. (Formula I, R=CH_3, R′, R‴ =Ph, R″=H).—Acetylphenylglycine (3·6 g.) and phenylhydrazine (2 g.) were heated in alcoholic solution (30 c.c.) on the water-bath for seven hours. The alcohol was evaporated off and the resulting oily mass was triturated first with dilute hydrochloric acid when it became solid and then with dilute sodium carbonate solution. Finally it was washed with a little ether. On crystallising now twice from alcohol rectangular plates, m.p. 163-164°, were obtained. (yield, 2·6 g.) (Found: N, 15·91. $C_{16}H_{15}ON_3$ requires N, 15·85 per cent.).

The triazine is insoluble in dilute as also in concentrated alkali solution. Dilute hydrochloric acid is without any action. It dissolves in concentrated hydrochloric acid but is reprecipitated on diluting with water. With concentrated sulphuric acid it gives an immediate and permanent bright rose-red colour. It is soluble in ethyl and methyl alcohols, benzene, chloroform, acetone, glacial acetic acid and ethyl acetate and insoluble in ether and ligroin.

Acetyl o-*Tolylglycine*.—o-Tolylglycine was prepared in the same manner as phenylglycine and the acetylation was carried out by heating with acetic anhydride at 180° in an oil-bath. (*Ber.*, 1892, **25**, 2270.)

2-*Phenyl*-5-o-*tolyl*-6-*methyl*-3-*ketotetrahydro*-α-*triazine*. (*Formula* I, (R = CH_3, R′=C_7H_7, R″ = H, R‴=Ph).—A solution of acetyl o-tolylglycine (5 g.) and phenylhydrazine (2·5 g.) in alcohol (40 c.c.) was refluxed for ten hours. The oily product obtained on removal of the solvent was washed successively with dilute hydrochloric acid and dilute sodium carbonate solution and finally crystallised from alcohol. Rectangular plates, m.p. 183-184°, were obtained (yield, 3·2 g.). (Found: N, 15·12. $C_{17}H_{17}O_3$ requires N, 15·05 per cent.).

Its behaviour towards acids and alkalis both dilute and concentrated resembles that of the previous compound.

Acetyl α-*Naphthylglycine*.—α-Naphthylglycine was obtained by heating α-naphthylamine and monochloroacetic acid with water on the sand-bath (*Ber.*, 1889, **22**, 2372). Treatment with acetyl chloride in the cold gave acetyl α-naphthylglycine (*Ber.*, 1892, **25**, 2290).

2-*Phenyl*-5-α-*naphthyl*-6-*methyl*-3-*ketotetrahydro*-α-*trazine*. (*Formula* I, R = CH_3, R′ = $C_{10}H_7$, R″ = H, R‴=Ph).—Acetyl

α-naphthylglycine (4·8 g.) and phenylhydrazine (2 g.) were heated in alcoholic solution (50 c.c.) on the water-bath for eight hours. The triazine was isolated after evaporating off the solvent and washing away the unacted upon reactants in the usual manner. Two crystallisations from alcohol gave fine scales, m.p. 221° (yield, 3·5 g.) (Found: N, 13·45. $C_{20}N_{17}ON_3$ requires N, 13·33 per cent.)

The triazine exhibited the same properties as the two previous compounds.

Condensation of Hippuric Acid with Phenylhydrazine.—An alcoholic solution of hippuric acid (5·4 g.) and phenylhydrazine (3·2 g). was heated under reflux for five hours. The product was isolated as usual by removing the solvent and the unaltered reactants, and recrystallised; a sample having a sharp melting point could not be obtained even on repeated fractionations from different solvents (alcohol, acetone, and ethyl acetate). The final fractions like the first fractions melted between 178 and 186°. (Found: C, 71·56; H, 5·44; N, 16·83. $C_{15}H_{13}ON_3$ requires C, 71·71; H, 5·17; N, 16·73 per cent.).

The product is insoluble in dilute acids and in dilute or concentrated alkalis. It dissolves in concentrated hydrochloric acid but is precipitated unchanged on dilution with water. With concentrated sulphuric acid it forms a rose-red solution almost immediately. It is soluble, easily in alcohol, acetone and glacial acetic acid, appreciably in ethyl acetate and sparingly in benzene, chloroform, ether and ligroin.

Hippuric Acid Phenylhydrazone (VI).—An aqueous solution of phenylhydrazine hydrochloride (2·5 g. in 50 c.c.), sodium acetate (6 g.) and hippuric acid (3 g.) were heated on the water-bath for three hours. The phenylhydrazone separated out after some time and was crystallised from alcohol in fine scales, m.p. 137-138°. (Found: N, 15·67. $C_{15}H_{15}O_2N_3$ requires N, 15·61 per cent.).

The phenylhydrazone is soluble in alcohol, acetone and acetic acid and insoluble in benzene, chloroform and ether. It dissolves in alkalis and decomposes on keeping for some months.

Ring-closure.—The phenylhydrazone (2 g.) was heated at 155-160° for half an hour. On crystallising twice from alcohol in presence of animal charcoal rectangular plates, m.p. 177-186°, were obtained. The m.p. was not depressed by admixture with a sample obtained directly from hippuric acid and phenylhydrazine.

Acetylglycine was obtained by heating glycine with acetic anhydride in benzene solution on the water-bath (*Ber.*, 1884, **17**, 1664).

Condensation with Phenylhydrazine.—Acetyl glycine (4·7 g.) was condensed with phenylhydrazine (4·3 g.) in the usual way. The product on crystallisation from alcohol melted at 200-206° and no improvement was observed in the melting point on crystallisation and recrystallisation of the different fractions from either alcohol or acetone. (Found: N, 22·34. $C_{10}H_{11}ON_3$ requires N, 22·22 per cent.)

Condensation of Hippuric Acid with asym.-*Phenylbenzylhydrazine.*

1-*Phenylbenzylamine-2-phenyl-5-iminazolone* (*Formula* V).—An alcoholic solution (40 c.c.) of hippuric acid (5 g.) and phenylbenzylhydrazine (5·5 g.) was refluxed on the water-bath for eight hours. The solvent was evaporated off and the viscous mass washed with dilute hydrochloric acid and dilute sodium carbonate solution. On crystallising from alcohol needles, m.p. 147°, were deposited (yield, 7 g.). (Found: N, 12·27. $C_{22}H_{19}ON_3$ requires N, 12·31 per cent.)

The iminazolone is insoluble in acids and alkalis both dilute and concentrated. With concentrated sulphuric acid a rose-red colour develops after a short time. It is soluble in alcohol, benzene, chloroform, acetone, acetic acid, and ethyl acetate and insoluble in ether and ligroin.

My sincerest thanks are due to Prof. P. C. Mitter, M.A., Ph.D., for his kind interest in the work throughout.

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A Method for Distinguishing Isomeric, Tautomeric, and Polymeric from Polymorphic Optically Active Substances.

By Bawa Kartar Singh.

That a chemical substance may exist in two (or more) mutually convertible modifications has been known for more than one hundred years. Although Smithson Tennant (*Phil. Trans.* 1797, **87**, 123) had shown as early as 1797 that diamond and charcoal consist of the same element carbon, it was not till 1814 that Humphry Davy (*ibid*, p. 557) accepted the correctness of this observation. But even after Mitscherlich (*Ann. Chim. Phys.*, 1822, **19**, 407) had noticed this phenomenon in sulphur and a few other substances, its appearance was still regarded as exceptional. At the present time, the number of such substances is very large. It is, however, uncertain whether the difference between them is due to a different molecular structure or configuration, or is to be interpreted as merely due to a different space lattice arrangement of the same chemical molecule. The former, in which the difference is one of chemical structure of the molecule, is classed as isomerism (including tautomerism and polymerism). The latter, in which the differences are brought about by different space lattice arrangement of identical molecules in the crystals, are grouped under polymorphism.

The two phenomena can be distinguished in the following simple way: If the modifications form a single independent component, they are polymorphic. The differences between them will be confined to the solid state only. When once the crystal structure is broken down, they will disappear. On the other hand, if the modifications form as many independent components, they are isomeric. The differences between them will persist in solution, unless tautomeric equilibrium has been established.

The methods, which have been employed for ascertaining the polymorphic or isomeric (including tautomeric) nature of the

modifications, depend on finding out whether the solutions given by them are identical or not. These methods will obviously fail in the case of tautomeric substances with a large velocity of change, as the solutions of the different modifications on account of tautomeric equilibrium will be identical. The tautomeric modifications will, therefore, appear as polymorphic.

Sidgwick (*J. Chem. Soc.*, 1915, **107**, 672) has made use of the above mentioned properties of the solutions of the two classes of substances, and has devised a method of diagnosis depending on the solubility. If to a saturated solution of the more soluble of two polymorphous modifications some of the other modification is added, the concentration of the solution will not increase, since the two forms give the same molecule in solution. If, on the other hand, the two forms are isomeric or tautomeric, the addition of the less soluble form will cause an increase in the concentration of the solution. As a measure of the concentration of the solution, Sidgwick determines the cryohydric point, using an ordinary Beckmann apparatus. The cryohydric points are determined for some suitable solvent for the two forms separately and then for the two forms together. If polymorphous, the mixture of the two forms will give a point lying between those of the separate forms ; but if isomeric or (tautomeric), the point given by the mixture will lie below that of the more soluble form, the depression of the freezing point by the two together approximating to the sum of the individual depressions.

It may be mentioned that Bruni (*R. Accad. Sci. Lett. Art. Padova*, 1910, **26**, 357) had anticipated Sidgwick's suggestion for the above mentioned method. He claims priority over Sidgwick (*J. Chem. Soc.*, 1915, **108**, *ii*, 827).

The study of the properties of solutions of polymorphous and isomeric modifications of optically active substances furnishes a much simpler but equally trustworthy method of distinguishing between them. From what has already been said, it is clear that the rotatory power of each of the polymorphous modifications will be identical, whereas it will be different in the case of isomeric or tautomeric forms. It is, however, possible for the rotatory dispersion curves of two different substances to intersect at a point corresponding to some wave-length, and thus indicate identical rotatory power for them for that wave-length. The result will be that the two modifications, which are isomeric, will

appear as polymorphous. In order to get over this ambiguity, rotatory dispersion should be measured. In the case of polymorphous forms, the values will be identical throughout the range of the spectrum investigated. On the other hand, these values will be different in the case of isomeric (or tautomeric) modifications. This method is necessarily only applicable to optically active substances, and is, therefore, not so general as the method of Bruni and Sidgwick. It has the advantage that, as it is much more rapid than that involving freezing point determination, the possibility of the two forms (if indeed they are not polymorphous) coming to tautomeric equilibrium in the course of the experiment, is greatly diminished. It has the further advantage that a much smaller quantity of the substance is required for the measurement of rotatory dispersion than for the measurement of the cryohydric point.

The above-mentioned principle has been successfully applied in the diagnosis of the three forms of *o*-iodophenyl-imino-*d*-camphor* melting at 97°, 93° and 87° respectively.

(α) The lowest-melting form is obtained on condensing *d*-camphorquinone and *o*-iodoaniline in the presence of anhydrous sodium sulphate at 80-85°. When the alcoholic solution is cooled undisturbed in an ice-bath, light yellow prisms, m.p. 87°, are deposited.

(β) The intermediate-melting modification is formed when the temperature of condensation is higher (90-97°). It is obtained as yellow prisms (m.p. 93°) by dissolving the product of condensation in the least possible quantity of hot alcohol, and stirring the solution during cooling. As is shown below, unlike the form (α), this form does not change into the form (γ) when heated alone even above its melting point (*e.g.* 95°).

(γ) The highest-melting form is obtained when a saturated alcoholic solution of the form of m.p. 87° (α) is boiled for a few

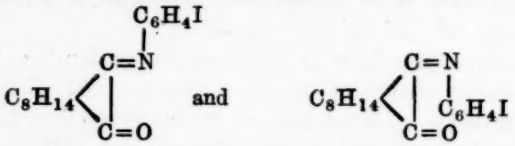
* These compounds will be more fully described in a separate communication, in which the analytical results agreeing with the formula $C_{16}H_{18}ONI$ for each modification will be given in support of the view that these three substances are chemical individuals. The conversion of the α-from into the γ-form with or without a trace of the latter and that of the β-form into the γ-modification only in the presence of a trace of the γ-form by heat shows that these forms are three distinct substances and not impure specimens of one and the same substance. This is also borne out by the identical values of their rotatory power in three solvents for three wave-lengths (see Table I).

minutes, cooled and precipitated with water. It is deposited as yellow prisms melting at 97°. It is, however, more conveniently obtained by heating for a few minutes the lowest melting form (α) or for a longer period the intermediate melting form (β) at 75°-80° with a trace of the highest-melting form (obtained from a previous operation) or by heating the lowest-melting form (α) alone near its melting point for a longer period. The reverse change by heat cannot be brought about:

$$\text{Form } (\alpha) \text{ or } (\beta) \xrightarrow[\text{at } 79°\text{-}80°]{\text{Heat (with a trace of the } \gamma \text{ form)}} \text{Form } (\gamma) \text{ m.p. } 97°.$$

It is thus clear that the β-modification is not a mixture of the two other forms, but is a definite third polymorphic modification of the substance.

The possibility of geometrical isomerism in the case of the different forms *o*-iodophenylimino-*d*-camphor is not excluded owing to the presence of the azethenoid group in the molecule, thus:



But the identical values for the rotatory power and rotatory dispersion of the three forms as given in Tables I and II definitely prove that those forms are polymorphous and not stereoisomeric.

TABLE I.

Specific Rotations of the Three Modifications of o-Iodophenylimino-d-camphor at 35°.

Length of tube = 2 dcm.

Modifications.	Solvent.	Concentration. (g. 100 c.c.)	[α] $Hg_{gr.}$	$Hg_{yell.}$	Na_D
γ	Chloroform	0·7228	268·4°	215·2°	206·7°
β	,,	0·7200	269·5°	216·7°	207·6°
α	,,	0·7204	265·9°	213·0°	204·°0
γ	Methyl alcohol	0·7220	249·3°	201·5°	189·0°
β	,,	0·7200	249·3°	200·7°	188·9°
α	,,	0·7228	249·1°	200·7°	188·2°
γ	Benzene	0·4860	298·4°	235·6°	220·2°
β	,,	0·7232	298·0°	237·2°	220·6°
α	,,	0·7244	297·5°	236·8°	220·9°

TABLE II.

Dispersion-ratios of the Three Modifications of o-Iodophenylimino-d-camphor at 35°.

Modifications.	Chloroform.		Methyl alcohol.		Benzene.	
	$\frac{[\alpha]_{Hg_{yell.}}}{[\alpha]_{Hg_{gr.}}}$	$\frac{[\alpha]_{Na_D}}{[\alpha]_{Hg_{gr.}}}$	$\frac{[\alpha]_{Hg_{yell.}}}{[\alpha]_{Hg_{gr.}}}$	$\frac{[\alpha]_{Na_D}}{[\alpha]_{Hg_{gr.}}}$	$\frac{[\alpha]_{Hg_{yell.}}}{[\alpha]_{Hg_{gr.}}}$	$\frac{[\alpha]_{Na_D}}{[\alpha]_{Hg_{gr.}}}$
γ	0·802	0·770	0·808	0·758	0·790	0·738
β	0·804	0·770	0·805	0·758	0·796	0·740
α	0·801	0·767	0·806	0·756	0·796	0·742
Mean	0·802	0·769	0·806	0·757	0·794	0·740

In Tabl I and II, Hg_{gr}, Hg_{yell}, and Na_D refer to the green mercury line 5461, the yellow mercury line 5780, and the yellow sodium line 5893 respectively.

The Effect of Polymorphism on Studies on the Relation of Optical Activity and Chemical Constitution.

When polymorphous substances are colourless and possess identical melting point, it is generally not an easy matter to differentiate between them. The substances may be chemically pure, but not physically so. The hitherto recognised physical or physico-chemical constants of solid substances are values which, in many cases, refer to metastable mixtures of two or more modifications of that substance in unknown proportions. Naturally no definite importance can be attached to the values of such constants, *e.g.*, density, refractive index, solubility, heat of solution, melting point, crystalline form, vapour pressure, etc. In the case of optically active polymorphous substances, the rotatory power is identical for the different forms. This constant will not, therefore, be vitiated as in other cases, by admixture with physically impure and metastable forms of the substance. It is, therefore, fortunate that the correlation of that esoteric property known as optical activity with the chemical structure of the molecule is, unlike other properties, unaffected by the phenomenon of polymorphism.

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